TECHNICAL REPORT 1973
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Environmental Security Technology Certification Program (ESTCP)

Project ER-0523

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ADMINISTRATIVE INFORMATION

The work described in this report was performed for the Environmental Security Technology Certification Program by the Environmental Sciences Branch (Code 71750), SPAWAR Systems Center Pacific.

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SB

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ACRONYMS AND ABBREVIATIONS

ΔC	Gradient in concentration
$\mu g\ cm^{-2}\ cleaning^{-1}$	Micrograms per square centimeter per cleaning
$\mu g\ cm^{-2}\ d^{-1}$	Micrograms per square centimeter per day
$\mu g\ g^{-1}$	Microgram per gram
$\mu g\ L^{-1}$	Micrograms per liter, same as parts per billion
µL	Microliter or a millionth of a liter
µm	Micrometer or a millionth of a meter
a	Activity
ADCP	Acoustic Doppler Current Profiler
BLM	Biotic Ligand Model
CBR	Critical Body Residue
CH3D	Curvilinear Hydrodynamics in Three Dimensions fate and transport model
CHESS	Chemical Equilibria in Soils and Solutions
CL	Confidence Limit
CTD	Conductivity, Temperature, and Depth profiler
Cu	Chemical symbol for copper
Cu-CC	Copper Complexation Capacity
Cu-ISE	Copper Ion-Selective Electrode
Cu^{2+}	Aqueous free copper ion
Cu_{diss}	Dissolved copper concentration
Cu_{part}	Particulate copper concentration
Cu_{tot}	Total copper concentration
CV	Coefficient of Variation
CWA	Clean Water Act
DGPS	Differential Global Positioning System
DLL	Dynamic Link Library
DoD	Department of Defense
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DO	Dissolved Oxygen
dw	Dry Weight
EC50	Water concentration producing a toxic effect to 50% of the population
ED50	Tissue concentration producing a toxic effect to 50% of the population
ECAM	Environmental Cost Analysis Methodology
ESTCP	Environmental Security Technology Certification Program
F&T	Fate and Transport
FIAM	Free Ion Activity Model
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
h	hour
HDPE	High Density Polyethylene
HEPA	High Efficiency Particle Air
ICP-MS	Inductively Coupled Plasma with Mass Spectrometry detection
km^2	Square kilometer
$kg\ y^{-1}$	Kilogram per year

LA50	Lethal accumulation level with a toxic effect to 50% of the population
LOEC	Lowest-observable-effect concentration
LOED	Lowest-observable-effect dose
m	Meter
M	Moles per liter
MΩ cm^{-1}	Mega-ohm per centimeter
MOS	Margin of Safety
MESC	Marine Environmental Survey Capability
mg L^{-1}	Milligrams per liter
mL	Milliliter, or a thousandth of a liter
mV	Millivolt, or a thousandth of a volt
nmol g^{-1}	Nanomole per gram
nmol g-dw^{-1}	Nanomole per gram dry weight
nmol g-ww^{-1}	Nanomole per gram wet weight
nmol mg C^{-1}	Nanomole per milligram of Carbon
NDCEE	National Defense Center for Environmental Excellence
NOEC	No observable effect concentration
NOED	No observable effect dose
NOM	Natural Organic Matter
NPDES	National Pollutant Discharge Elimination System
ONR	Office of Naval Research
pCu	Negative logarithm of the free aqueous copper ion activity ($-\log a\,Cu^{2+}$)
PHNS&IMF	Pearl Harbor Naval Shipyard & Intermediate Maintenance Facility
POC	Particulate Organic Carbon
ppb	Parts per billion, same as µg L^{-1}
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
sd	Standard deviation
SERDP	Strategic Environmental Research and Development Program
SRM	Standard Reference Material
SSC Pacific	Space and Naval Warfare Systems Center Pacific
TMA	Trace Metals Analyzer
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UV	Ultraviolet
USACE	United States Army Corps of Engineers
U.S. EPA	United States Environmental Protection Agency
WHAM	Windemere Humic Aqueous Model
WES	Waterways Experiment Station
WER	Water-Effect Ratio
WERF	Water Environment Research Federation
WQC	Water Quality Criteria
WQS	Water Quality Standards
ww	Wet weight

EXECUTIVE SUMMARY

Site-specific Water Quality Standards (WQS) are developed to reach regulatory criteria appropriate for individual bodies of water. A nationally suggested Water Quality Criteria (WQC) for seawater was derived with laboratory water (i.e., clean coastal seawater) that does not include the natural ingredients that provide buffering of toxic effects by contaminants. As such, federal WQC could in many cases be overprotective relative to the level of protection that is intended by current EPA guidelines. In such situations, it would require the achievement of regulated effluent characteristics that are very difficult and expensive to attain. The regulatory community overcame this problem with the development of WQS, TMDLs, and WERs. However, these approaches require long-term, demanding, and expensive studies. To speed up the development of WQS, the U.S. EPA recently incorporated the copper (Cu) BLM into a freshwater WQC (U.S EPA, 2007). This model considers the natural characteristics of each body of water in predicting a site-specific WQC for a particular body of water. In a similar effort, the regulatory community is supporting the development of a seawater-BLM for the development of WQS.

Fate and transport (F&T) models are used for the understanding and prediction of the fate of contaminants in coastal bodies of water. The Curvilinear Hydrodynamics in Three Dimensions (CH3D) was developed at the U.S. Army Corps of Engineers (USACE) Waterways Experiment Station (WES) to simulate physical processes in bays, rivers, lakes, and estuaries under the forcing of tides, wind, and freshwater inflows. The general acceptance of the validity and utility of this model is demonstrated by its wide use in the regulatory and environmental communities, in part because of its amenability to integration with other models.

The objective of this work is the development and validation of a model integrated by the F&T model CH3D and the seawater-BLM for the simulation of transport, distribution, and fate, and potential toxicity of copper in Department of Defense (DoD) harbors. The integrated model will predict high-resolution distributions of WQS based on scientific observations, providing relief to the user and achieving the level of protection intended by the regulatory community. As this model is based on loading sources, it will also work as a management tool for effluent controlling measures.

The demonstration of the integrated model in San Diego Bay fulfilled most of the performance objectives. These objectives included a reliability parameter for predicting copper chemical species, including total (Cu_{tot}), dissolved (Cu_{diss}), and free copper ion (Cu^{2+}). The integrated model was calibrated using data from four sampling cruises (30 August 2000, SD26; 30 January 2001, SD27; 27 February 2002, SD33; and 14 May 2002, SD35), and validated with data from two other sampling cruises (11 May 2001, SD31; 19 September 2001, SD32) from the Strategic Environmental Research and Development Program (SERDP) project CP-1156. Cu_{tot} concentrations predicted by the integrated model explain 74 to 93% of the variability of the measured values, which fulfills the performance objective of explaining ≥60% of the variability in the field data. Similarly, for Cu_{diss}, the integrated model predictions explain 68 to 92% of the variability of the measured values.

Data collected by Earley et al. (2007) were used in the demonstration of the integrated model in Pearl Harbor. The events of 15–18 March 2005 (Event 1), 18–20 October 2005 (Event 2), and 15–19 May 2006 (Event 4) were used for calibration and validation. The event of 23–27 January 2006 (Event 3) is the only one for the wet season, and was only used for calibration.

Demonstration of the integrated model in Pearl Harbor for the prediction of Cu_{tot} was successful. Predicted Cu_{tot} explain 61 to 94% of the variability of the measured concentrations. In the case of Cu_{diss}, the predictive capability of the integrated model was affected by the presence or absence of a minimal gradient in concentration. In the cases where there was a gradient in concentration (ΔC) of

0.22 µg L^{-1} or greater, the predicted values explain 72 to 77% of the variability. In contrast, in those cases where the range in Cu_{diss} was minimal (ΔC 0.009 µg L^{-1}), making Cu_{diss} essentially a constant value, the utility of the integrated model for prediction of the spatial variation in measured concentrations was negated.

In contrast, the performance objective for the prediction of free copper ion (Cu^{2+}) was not met. In San Diego Bay, field measured Cu^{2+} was extremely stable and constant; this situation is similar to having a small ΔC, and neglects the use of the statistical method applied to both Cu_{tot} and Cu_{diss}. Linear regression cannot be applied for the case of a constant variable. However, comparison of the predicted with the field data indicates that the predicted values are within an order of magnitude of the measured values for most of San Diego Bay, excluding the area by the mouth of the Bay. There are no measurements of Cu^{2+} in Pearl Harbor; therefore, no procedure was available to evaluate the predictive capability of the integrated model.

Regulatory use of the integrated model will be on the prediction of toxicity and WQS following a harbor-wide approach. For San Diego Bay, toxicity predictions are within the expected performance criteria, as 87% of the values predicted for calibration and validation are within a factor of two of the measured values. For Pearl Harbor, 87% or better of the predicted toxicities are within the factor of two of measured values. Two advantages of applying the integrated model over the current approach of developing toxicity and WER studies are the spatial resolution of the predicted values and the marked reduction in field and laboratory effort. The integrated model provided high-resolution (≈100 m) geographical distributions of toxicity and WER, which can only be developed by the inclusion of an impractically large number of samples when following the recommended WER approach.

Application of the integrated model for the development of WQS results in significant relief, while maintaining the level of environmental health intended by the regulatory community. WERs predicted by the integrated model for San Diego Bay and Pearl Harbor are comparable to those previously measured, as 80 and 98% of the cases for both calibration and validation are within a factor of two of the corresponding measured values, respectively. A geometric mean WER of 1.48 and 1.17 were predicted for San Diego Bay and Pearl Harbor, respectively, which are within the range previously reported. Application of a mean WER for each area in San Diego Bay results in significant relief, with an average WQS of 5.0 µg L^{-1} for the whole Bay.

Implementation of the integrated model in a new harbor will result in lower costs than those required for existing processes. The costs for this demonstration of the integrated model are compared to the costs expected from the individual implementation of a WER and an F&T model in a harbor of similar dimensions and characteristics as San Diego Bay. While this comparison is justified by the fact that both processes are required to provide information similar to that generated by the integrated model, the costs predicted for implementation of these processes was simplified to some degree. Moreover, a significant increase in effort should be expected in order for these processes to provide the same quality on spatial information and capability for forecasting effects. The cost of the demonstration in San Diego Bay was $580,000, which was $250,695 more than the costs estimated for implementation of a WER and a CH3D ($329,305). However, implementation of the integrated model in a new harbor is estimated at $189,567, which will provide better temporal and spatial resolution and forecasting capability of source controls.

This demonstration contributes to the transition of this technology to the user community by providing a clear example of implementation at real-world DoD sites. Critical aspects of this contribution include development and refinement of the BLM for sensitive saltwater toxicity endpoints and implementation of U.S. EPA guidance for TMDLs and site-specific WQS within a rigorous numerical modeling framework for Cu and eventually other metals.

CONTENTS

Figures

Tables

1. INTRODUCTION

1.1 BACKGROUND

There is a growing Department of Defense (DoD) requirement for the development of site-specific Water Quality Standards (WQS) and scientifically defensible Total Maximum Daily Loads (TMDLs) to achieve compliance of copper (Cu) point source and non-point source discharges to harbors. Copper is one of the ubiquitous contaminants found in industrial and non-point source effluents that enter the marine environment, including those from DoD activities, such as shipyards, stormwater, and ships (Nriagu, 1996; Johnson, Grovhoug, and Valkirs, 1998; Seligman and Zirino, 1998; Zirino and Seligman, 2002). Because of its wide use as a biocide in antifouling coatings and in piping systems, Cu is a particularly prevalent contaminant in and around DoD pier areas, shipyards, marine facilities, and harbors. Copper in the marine environment is regulated under the Clean Water Act (CWA) at levels that generally do not recognize site-specific complexation of copper that controls toxicity (United States Environmental Protection Agency, U.S. EPA, 1997). Strict application of copper WQS at DoD facilities without accounting for site-specific factors has led to difficulties in compliance with the resulting discharge permits, and disproportionate cost requirements for containment and/or treatment systems.

Development of site-specific WQS and TMDLs are closely linked. Site-specific WQS dictate the understanding of copper bioavailability in local waters, while TMDLs require the understanding of loading terms, mass balance and assimilation capacity of a particular water body (U.S. EPA, 1999a). TMDL actions are generally triggered when a water body is designated as impaired based on ambient water concentrations exceeding the WQS. Thus, the development of site-specific WQS can strongly influence the designation of impairment and the subsequent requirement for TMDLs. For example, in San Diego Bay, ambient copper concentrations approach or exceed the U.S. EPA Water Quality Criteria (WQC) and the state WQS (3.1 $\mu g\ L^{-1}$, U.S. EPA, 1997; Katz, 1998; Chadwick et al., 2004; Blake, Chadwick, Zirino, Rivera-Duarte, 2004); however, toxicity studies suggest that ambient concentrations would not result in toxicity or exceed a site-specific WQS after the application of a water-effect ratio (WER) (Rosen, Rivera-Duarte, Kear-Padilla, and Chadwick, 2005). A different situation occurred in Pearl Harbor, where ambient copper concentrations are well below the WQC ($0.62 \pm 0.25\ \mu g\ L^{-1}$, average ±1 standard deviation) (Earley et al., 2007); but, discharges at the Pearl Harbor Naval Shipyard and Intermediate Maintenance Facility (PHNS&IMF) were regulated to a WQS of 2.9 $\mu g\ L^{-1}$. Implementation of actions to derive WQS for Pearl Harbor demonstrated that that level of regulation was overprotective (Earley et al., 2007). Implementation of a site-specific WQS in both cases could reduce the likelihood of TMDL actions.

The present U.S. EPA WQC justifiably fulfill their mission of protecting the environment, but generally do so from a scientific basis that does not account for site-specific factors that regulate bioavailability and toxicity, and thus are often overprotective (Seligman and Zirino, 1998; Zirino and Seligman, 2002) relative to the level of protection intended by the guidelines (Stephan et al., 1985). In recognition of this conservatism, the effects of copper speciation and bioavailability in seawater are addressed indirectly by the regulatory community via the adoption of a number of mechanisms. These mechanisms include using dissolved copper (Cu_{diss}) rather than total recoverable copper (Cu_{tot}) concentration (Metals Translator) (U.S. EPA, 1996a), and using WER (U.S. EPA, 2001). This is a multiplier of the national ambient WQS, which is derived from the ratio between the toxicity observed in the regulated body of water and that from laboratory water used for the development of the federal WQC. While these empirical strategies provide one pathway for implementation of site-specific WQS and discharge permits, they are often expensive to employ and do not provide a strong technical basis for addressing the complete range of factors that influence transport, fate, and effects.

As an alternative, copper speciation and bioavailability in freshwater systems have been addressed by using the Biotic Ligand Model (BLM) (Di Toro et al., 2001; Santore et al., 2001; U.S. EPA, 2007) to derive a site-specific WQC. The BLM, which is based on evidence that mortality occurs when the metal-biotic ligand complex reaches a critical concentration, considers site-specific water quality characteristics to predict this critical concentration. The BLM-based approach has the potential to be more cost effective and easier to implement than the WER approach as a way to evaluate site-specific WQS for metals in seawaters.

1.2 DEMONSTRATION OBJECTIVES

Our objective is to demonstrate an integrated modeling system that will provide an improved methodology for achieving compliance for copper in DoD harbors (i.e., developing TMDLs, site-specific WQS, and WERs) in a manner consistent with the current regulatory framework recently released for copper in freshwater systems (U.S. EPA, 2007). The proposed system will also provide a management tool for the optimization of efforts on source control, as it will be robust enough for forecasting effects on copper concentration and the potential for toxicity in the harbor because of these efforts. The integrated model will include a hydrodynamic fate and transport (F&T) algorithm (i.e., Curvilinear Hydrodynamics in Three Dimensions [CH3D] model) and a copper toxicity sub-model (i.e., seawater-BLM) for simultaneous evaluation of F&T and potential effects of copper on a harbor-wide scale. This integrated modeling system was demonstrated by applying it to San Diego Bay, California, and Pearl Harbor, Hawaii. Results of this demonstrated technology could reduce control and treatment costs through more appropriate, site-specific WQS and discharge limits while maintaining the level of environmental protection required by current regulation. In addition, the development of copper toxicity parameters for the implementation of the seawater-BLM should provide WQS that better represent the actual environmental characteristics of the harbor and reduce requirements for costly empirical studies.

1.3 REGULATORY DRIVERS

Federal regulations that motivate developing site-specific WQS and scientifically defensible TMDLs include the WQC (U.S. EPA, 2007) and the National Pollutant Discharge Elimination System (NPDES) program, which was developed under the CWA to eliminate or reduce pollutant inputs to aquatic systems by imposing concentration limitations on discharges.

DoD drivers for the development of whole-harbor models for the control and management of loading sources include the following environmental requirements from the U.S. Navy Environmental Sustainability Development to Integration (NESDI[1]) program:

(2.II.02.e) Improvements in Three Dimensional Models of Contaminant Fate and Effects in the Marine Environment

(2.II.02.b) Improved Field Analytical Sensors, Toxicity Assays, Methods, and Protocols to Supplement Traditional Sampling and Laboratory Analysis

(2.II.01.k) Control/Treat Nonpoint Source Discharge

(2.II.01.q) Control/Treat Industrial Wastewater Discharges

[1] http://www.nesdi.navy.mil/Home.htm

The ultimate product from the demonstration of the integrated model in San Diego Bay and Pearl Harbor is the prediction of WQS in the form of a WER. For San Diego Bay, the WERs predicted by the model have a geometric mean of 1.47, and range from 0.57 to 3.24. A geographical gradient with predicted WERs of about 1.4 exist in the area of San Diego Bay influenced by coastal waters (mouth), increasing to a maximum of 3.24 in the back of the bay. These values are comparable to the range of 1.54 to 1.67 reported by Rosen et al. (2005). In Pearl Harbor, the predicted WER has a geometric mean of 1.17, with a range from 0.73 to 2.87. Comparison with measured WERs for San Diego Bay and Pearl Harbor indicate that the WERs predicted by the integrated model are within the expected performance criteria, with 88% of the values agreeing within a factor of two of the measured values.

1.4 STAKEHOLDER/END-USER ISSUES

These demonstrations contribute to the transition of this technology to the user community by providing a clear example of implementation at real-world DoD sites. Critical aspects of this contribution include development and refinement of the BLM for sensitive saltwater toxicity endpoints, and implementation of U.S. EPA guidance for TMDLs and site-specific WQS within a rigorous numerical modeling framework for copper and eventually other metals. Potential users will have the opportunity to find out the level of relief potentially achievable with a WER study, at a more affordable price. In addition, the developed integrated model will provide the capability to evaluate for the best possible remedial action in case of exceeding standards. In the San Diego Bay area, DoD users that could benefit directly from this demonstration include Navy Region Southwest (NAVFAC SW Division) and the facilities they support, including Naval Station San Diego, North Island Naval Air Station, and Subase San Diego. DoD users that could benefit directly from this demonstration in the Pearl Harbor area include Naval Station Pearl Harbor, PHNS&IMF, Hickam Air Force Base, Tripler Medical Center, Ford Island, Camp Smith Marine Corps Base, Manama Pearl City, Naval Magazine West Loch, and Naval Computer and Telecommunications Area Master Station, Pacific.

2. TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

The demonstrated technology is a direct transition from the Strategic Environmental Research and Development Program (SERDP) project CP-1156, "Determining the Fate and Ecological Effects of Copper and Zinc Loading in Estuarine Environments: A Multi-disciplinary Program." This technology integrates two primary components: (1) a CH3D numerical hydrodynamic F&T model that tracks the sources and simulates transport, distribution, and fate of copper, and (2) a seawater-BLM toxicity model that simulates the chemical speciation, competition, exposure, and response of sensitive marine organisms to the different forms of Cu, including the aqueous free copper ion (Cu^{2+}).

Fate and Transport Modeling. CH3D is a boundary-fitted finite difference, Z-coordinate F&T model developed at USACE WES (Johnson et al., 1991) to simulate physical processes in bays, rivers, lakes and estuaries (Wang and Martin, 1991; Wang, 1992; Wang and McCutcheon, 1993; Johnson, Wang, and Kim, 1995; Wang, Johnson, and Cerco, 1997; Johnson, Grovhoug, and Valkirs, 1998). The model simulates hydrodynamic currents in four dimensions (x, y, z, and time) and allows for the prediction of F&T of metals, fecal coliforms, and other contaminants in estuaries and coastal environments under the forcing of tides, wind, and freshwater inflows[2] (Sheng, Eliason, Chen, and Choi, 1991). The model has been applied to many Navy–U.S. EPA joint projects, including the Environmental Investment TMDL project for Sinclair Inlet, Washington;[3] the Uniform National Discharge Standards Program for ship discharges in Norfolk, Virginia; and the NPDES permit study for PHNS&IMF. The San Diego Bay grid covers approximately 215 km^2, with about 7000 grid elements and a resolution of approximately 100 meters. The Pearl Harbor grid covers 20.4 km^2, with 2342 grid elements and a resolution from about 50 to 200 meters (Figure 1).

The CH3D model allows for specific application enhancements. Some of these enhancements include adding a sediment transport model (CH3D-SED) and a cohesive sediment transport model (CH3D-COSED) to extend its utility to study problems involving changes in the bottom contour of rivers and channels. For this study, the enhancement was a seawater-BLM for predicting toxic effects of copper and WER parameters for bay waters.

Toxicity Modeling. The BLM of metal toxicity to aquatic organisms is based on the evidence that mortality occurs when a pre-defined metal–biotic ligand complex reaches a critical concentration (Di Toro et al., 2001; Santore et al., 2001). It is convenient to consider the site of action of metal toxicity as a biotic ligand, and in the case of freshwater fish, the proximate site of action of toxicity for metals such as copper or silver is the gill (Wood, 2001). Specifically, the immediate site of action of toxicity is understood to be the enzyme systems that reside in the gill, systems involved in iono-regulation, a life-sustaining process by which aquatic organisms maintain the ionic composition of their blood and other internal fluids in the presence of marked differences relative to their environment. It is similarly assumed for other freshwater and saltwater organisms, as a first approximation, that analogous physiological processes and enzyme systems are involved in ionoregulation and can be modeled with a similar framework.

[2] P. F. Wang and K. Richter. 1999. "A Hydrodynamic Model Study using CH3D for Sinclair Inlet." SSC San Diego technical report to Puget Sound Naval Shipyard. Contact authors at SSC Pacific, San Diego, CA.
[3] Ibid.

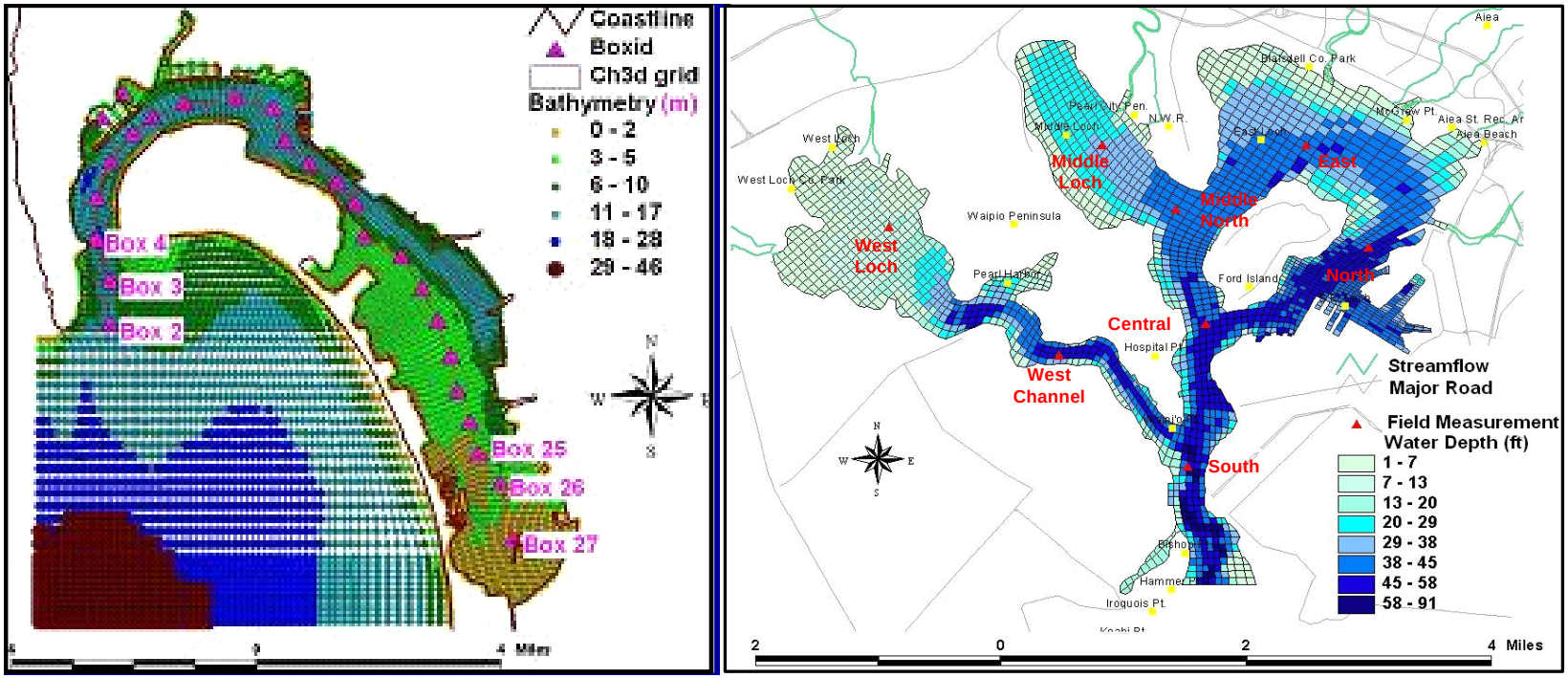


Figure 1. Modeling grid and bathymetry for San Diego Bay, California (left), and Pearl Harbor, Hawaii (right).

The biotic ligand interacts with the metal ions in solution, and the amount of metal that it binds is determined by a competition for metal ions with other aqueous ligands (Figure 2), particularly dissolved organic matter (DOM), and the competition for the biotic ligand between the bioavailable forms of the stressor metal and the other cations in solution.

The BLM for freshwater organisms has been well documented and tested (Figure 2, left panel). The model is an adaptation of the free ion activity model (FIAM), which posits that the free metal ion is correlated to toxicity (Morel, 1993; Campbell, 1995). The model is implemented using a chemical description of metal-DOM interactions developed for the Windemere Humic Aqueous Model (WHAM) (Tipping, 1994), with the WHAM formulation simulated within the Chemical Equilibria in Soils and Solutions (CHESS) model (Santore and Driscoll, 1995). It has been applied for copper, zinc, cadmium, lead, and silver for fish and invertebrates in freshwater, and for copper, using larval *Mytilus spp*. (mussel) in saltwater. The BLM is amenable for use in the context of TMDLs and regional risk assessments and within a probabilistic framework. As a result of extensive calibration and validation efforts, as well as the scientifically rigorous conceptual basis for the model, the copper BLM has been incorporated into a freshwater WQC (U.S. EPA, 2007).

Previous efforts to apply the freshwater-BLM to marine organisms provided promising results for estuarine conditions, but not for marine conditions. Both of these results are shown in Figure 3, where the freshwater-BLM predicted copper toxicity to *M. edulis* (blue or bay mussel) in waters from estuaries around the U.S. is compared to measured copper toxicity. In this figure, a solid line indicates the response for perfect agreement, and dashed lines indicate the area of agreement within a factor of two. The model predictions for a number of estuaries, including San Francisco Bay, Puget Sound, Galveston Bay, and Narraganset Bay are within the factor of two accepted by U.S. EPA for the freshwater BLM (Erickson, Benoit, and Mattson, 1987; U.S. EPA, 2007). However, these efforts to apply the model to marine organisms used biotic ligand parameters that were developed from freshwater chemical speciation and biological uptake and response for freshwater fish. This extrapolation from freshwater to marine systems was necessary because of the lack of good experimental data quantifying copper speciation, accumulation, and response for marine water and organisms. The use of freshwater parameters resulted in a reproducible bias when applied to marine waters collected in open ocean waters. The results for Pacific Ocean samples (blue squares) in Figure 3 indicate that the model consistently predicts copper EC50 values that are too low, compared with measured copper toxicity in these samples.

In this project, the seawater-BLM benefited from independent data collected from marine waters and organisms (Rosen et al., 2008) for development of the appropriate parameter values for a marine model. This implementation of the BLM does not use empirical correlations, instead it is based on a mechanistic thermodynamic description of seawater-specific metal-DOM binding, and organism-specific uptake and response. This description, including reaction stoichiometry and thermodynamic constants, was developed using measured copper speciation from complexation titrations in San Diego Bay water samples that were completed during SERDP Projects CP-1156 (Rivera-Duarte et al., 2005). Larval accumulation and response studies with sensitive marine organisms were completed as part of this project to provide realistic seawater toxicity parameters for the BLM that do not rely on empirical correlations extrapolated from freshwater (Rosen et al., 2008). The BLM was re-formulated to use these reactions and parameters, and then used to simulate copper chemistry, bioavailability and toxicity for comparison (as a field validation) with measurements in San Diego Bay and Pearl Harbor.

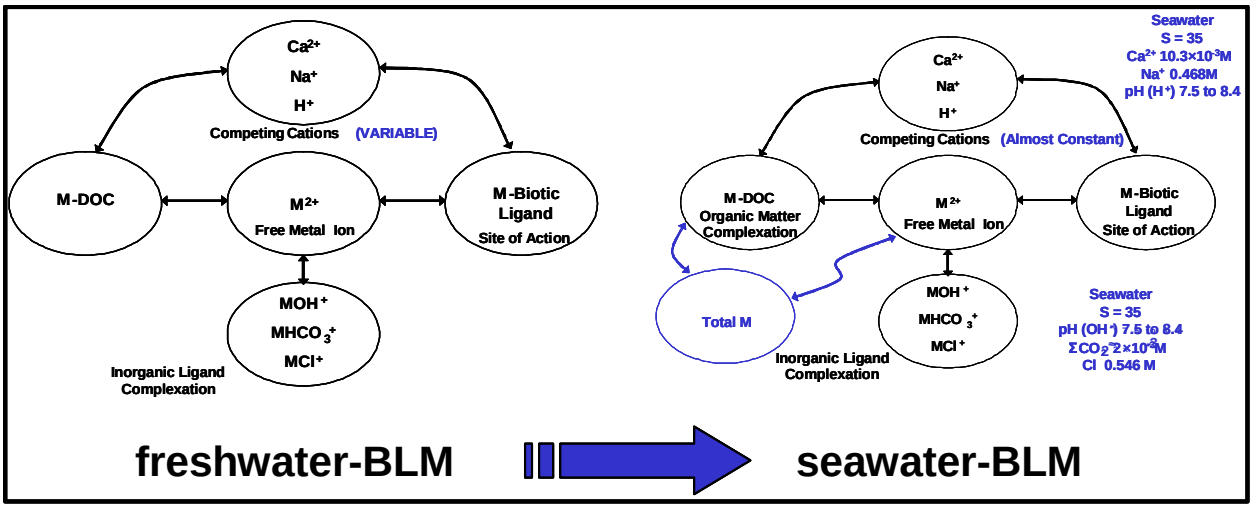


Figure 2. Schematic diagram of the structure of the BLM model and the requirements between the existing freshwater model (left side) and the emerging seawater model (right side).

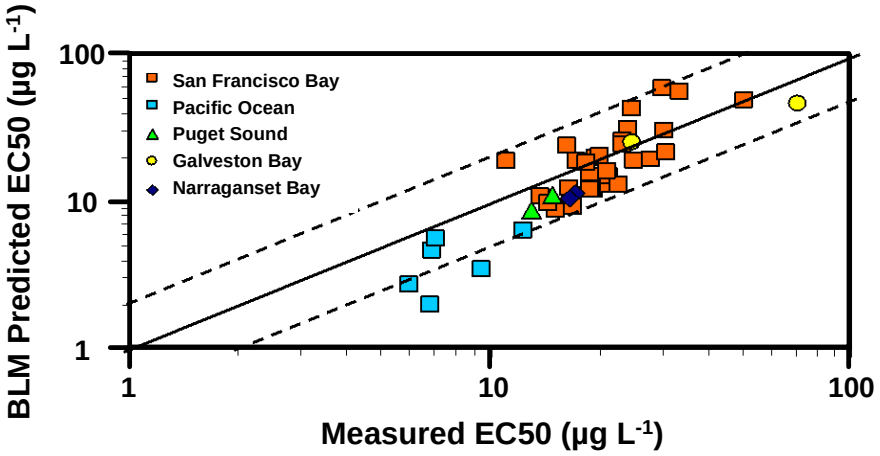


Figure 3. Comparison of freshwater-BLM predicted copper toxicity to measured values in estuaries from around the U.S. The solid line represents the one to one ratio, and the broken lines encompass a factor of two.

Integrated Model Demonstration. The fundamental innovation of this demonstration is integrating the F&T model CH3D with the seawater-BLM, both being state-of-the-science products, which provides a complete framework for simultaneously evaluating F&T and potential effects of copper on a harbor-wide scale. The need for this innovative integrated model is increasingly driven by regulatory requirements to achieve compliance for point source discharges, and to develop TMDLs and site-specific WQS. The integrated model also provides a tool for the optimization of effluent control measures and furthers the development of the seawater-BLM.

2.2 PREVIOUS TESTING OF TECHNOLOGY

The demonstration represents a natural extension of research and development efforts that have been supported by the Office of Naval Research (ONR), SERDP, the Water Environment Research Federation, HydroQual, Inc., and others that have been recently summarized in a review document developed from the 2001 ONR Copper Workshop (Zirino and Seligman, 2002).

Field data developed for the SERDP project CP-1156 was used for the development of the CH3D model in San Diego Bay. These data have been documented in a series of recent manuscripts including a description of the field program (Blake et al., 2004), methods (Rivera-Duarte and Zirino, 2004), mass balance (Chadwick et al., 2004), WER application (Rosen et al., 2005), and bioaccumulation factors (Rosen et al., 2008). Field data for the demonstration at Pearl Harbor is a direct result of the Copper Water Compliance Studies at PHNS&IMF performed by a scientific team from Code 71750, Environmental Sciences and Applied Systems, Space and Naval Warfare Systems Center Pacific (SSC Pacific), Puget Sound Naval Shipyard, and Atlantic Division Naval Facilities Engineering Command (Earley et al., 2007). Development of the BLM, primarily for application to freshwater species, has been documented in a series of publications, including a historical overview (Paquin et al., 2002a), technical basis (Di Toro et al., 2001), application to acute copper toxicity in freshwater fish and Daphnia (Santore et al., 2001), and application to silver toxicity in fish and invertebrates (Paquin et al., 2002b; 2007; Bielmyer et al., 2007). U.S. EPA has recently proposed using the BLM in freshwater based on research to validate it as an alternative to the WER method currently used (U.S. EPA, 2007).

2.3 FACTORS AFFECTING COST AND PERFORMANCE

Cost analysis for the demonstration is based on an assessment of the tasks expected to be required for future application at a previously un-modeled site. These tasks include model setup, calibration, execution, and validation. Specific cost data and estimates are compiled for these tasks. Although cost savings could vary significantly from site to site, an assessment of the potential costs for developing site-specific standards and TMDLs on a harbor-wide basis without the benefit of these models is also estimated.

Costs for regulatory discussion and acceptance are predicted. As this technology is directly associated with achieving regulatory compliance, the costs associated with presenting and discussing the results from this demonstration to the U.S. EPA are included. These costs are predicted assuming a minimum number of meetings at U.S. EPA headquarters in Washington, DC, with a maximum number of participants. However, these costs should not be further considered, as the process of acceptance of the seawater-BLM for full-strength seawater conditions by the U.S. EPA is almost completed.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The integrated model provides a cost-efficient approach for regulatory assessment and pollution control in DoD harbors. One advantage of the integrated model is that it is a more efficient approach than the traditional measurement program approach, since the initial costs of toxicity testing, seawater-BLM calibration, and integration of the seawater-BLM with CH3D will not have to be repeated for future applications in other DoD harbors. The more expensive traditional technologies for regulatory purposes and estimation of copper loads and toxicity in harbors include environmental monitoring and development of WERs, TMDLs, and mass balance models. Another approach for regulatory purposes is the implementation and measurement for load scenarios; however, this approach does not always consider the natural physical, toxicological, and chemical characteristics of harbors, factors that are fully considered in the integrated model. The integrated model also has advantages to the regulatory approach of application of total and dissolved copper-based standards. Adequate scientific evidence has shown that the free ion is the principal parameter for evaluation of toxic effects in aquatic environments, and the integrated model intrinsically relates toxicity to the free ion concentration. Another advantage is that the model should be relatively easy to implement in other harbors, where it could be applied with an optimized approach to data requirements. As CH3D

is a model commonly used by the regulated community, the implementation and use of the integrated model should be relatively easy. Another advantage of CH3D is its capability for enhancement, which is for the inclusion of subroutines for specific purposes, and the seawater-BLM that was relatively easy to integrate into the model. An advantage of the integrated model for management is that it provides predictive capability for pollution control scenarios, including optimized effluent management. It will also allow for the assessment of load allocation scenarios required for a TMDL regulatory approach. The integrated model also has the advantage of providing the basis/framework for the assessment of the F&T and effects of other contaminants in DoD harbors.

The limitations of the integrated model are related to the range of environmental conditions in DoD harbors. The model was only calibrated for two saltwater species (i.e., the larval life stage of the blue mussel and purple sea urchin), and while these species are among those most sensitive to copper, there could be other species that are more significant for other harbors. Note, however, that the larval blue mussel is among the species included in this analysis and that this organism is the most sensitive to copper in the U.S. EPA marine database. Normally, WQC developed by U.S. EPA are not based on the most sensitive organism, but because of the commercial importance of blue mussels, the marine water quality criterion is based on the sensitivity of this organism. While it is true that other DoD harbors may have other marine organisms that have not been tested in this analysis, the inclusion of the blue mussel in this work makes the calibrated model generally applicable as an alternative approach for deriving site-specific WQC in all marine environments.

A parameter considered of supreme importance for the regulation of toxicity in harbors is dissolved organic carbon (DOC) (e.g., Arnold, 2005; Arnold, Cotsifas, Corneillie, 2006). As the quantity and quality of DOC could vary spatially and temporally in any harbor, the model will require some calibration and validation in any other harbor. The natural variation of environmental parameters will require some data collection and/or estimation of un-modeled parameters required for the integrated model. A limitation to the integrated model could arise in those small harbors or limited areas of impairment where the costs of calibration and validation of the model outweigh those for traditional assessments.

Probably the most important current limitation is that regulatory acceptance of the seawater-BLM is still in process. Results from the final calibration and validation of the seawater-BLM were presented to personnel from the U.S. EPA, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division on 14 April 2008. At this meeting, it was accepted that the seawater-BLM is ready for inclusion for full-strength seawater regulation. The final procedures for its inclusion are expected to be completed by December 2008. A draft document for the inclusion of the seawater-BLM for regulatory use could be achieved by 2010.

3. DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The performance of the demonstrations were evaluated based on direct comparison of the model results to measurement data obtained from the SERDP project CP-1156 studies in San Diego Bay and the Copper Water Compliance Studies in Pearl Harbor (Earley et al., 2007). These studies provided a quantitative benchmark for judging the performance of the integrated model. Close correspondence between measured and predicted concentrations and toxicity thresholds are an indicator of project success. The performance objectives for these demonstrations are shown in Table 1.

The level of precision in the predictions is the result of the propagation of errors throughout the modeling. Quantitative performance objectives established for the prediction of Cu_{tot}, Cu_{diss}, and Cu^{2+} account for expected uncertainties associated with error propagation for the underlying F&T and speciation models. These errors arise from uncertainties in the quantification and prediction of source strength, water levels, water velocities, partitioning, and sediment exchange, among other factors. The highest precision is observed when physical parameters such as tides and currents are modeled. Precision declines when less precise parameters such as sources and sinks are included. The inclusion of chemical parameters further decreases the precision of the prediction. The rationale for selecting a performance objective of 60% (variance explained) for these predictions is based on professional judgment from previous modeling efforts. For example, Chadwick et al. (2004) report similar comparisons between field data and modeled predictions for Cu_{tot}, particulate copper (Cu_{part}), and Cu_{diss} that explain 91, 73, and 88% of the variance in the field data, respectively. The same data were used to evaluate the performance of the integrated model, and similar metrics were expected.

Quantitative performance objectives for prediction of toxicity and WERs must account for all of the uncertainties described above, as well as uncertainties associated with the organism uptake and response. Experience with the freshwater-BLM is that predictions within a factor of two are achievable when the model is properly parameterized and uses the water quality characteristics of the toxicity test water (Erickson, Benoit, and Mattson, 1987). This level of certainty has been sufficient for regulatory acceptance of the freshwater-BLM (U.S. EPA, 2007).

Qualitative performance objectives for the integrated model stability and computational time are consistent with current levels of stability for the independent models, and establish a benchmark for improved computational efficiency when running the integrated model versus running the models independently.

3.2 TEST SITE SELECTION

The main criterion for selection of the harbors for the demonstration is that they must sustain a significant use by the DoD. Both San Diego Bay and Pearl Harbor meet this criterion as they are heavily used by the Navy. Navy bases located in the San Diego Bay area include Naval Air Station, North Island; Naval Amphibious Base, Coronado and Imperial Beach; Fleet Anti-Submarine Base; Naval Station San Diego; Submarine Base, Old Town Campus; Broadway Complex; and Naval Medical Center, Balboa. Navy, Air Force, and Marine installations located in Pearl Harbor include Naval Station Pearl Harbor; PHNS&IMF; Naval Submarine Base; Hickam Air Force Base; Tripler Medical Center, Ford Island; Camp Smith Marine Corps Base, Manama Pearl City; Naval Computer and Telecommunications Area Master Station, Pacific; and Naval Magazine West Loch. The second criterion for selecting the harbors is the availability of the environmental information required by CH3D and the seawater-BLM. This information is available for San Diego Bay, in part, as a direct

result of project CP-1156 supported by SERDP. Results of that effort include a geographical and temporal description of the environmental conditions in San Diego Bay, chemical speciation and distribution of copper, toxicity of copper to mussels and purple sea urchin, and WER calculations. Required environmental information is available for Pearl Harbor as a direct result of the Copper Water Compliance Studies at PHNS&IMF to develop site-specific water quality objectives in support of NPDES permit negotiations (Earley et al., 2007). Results of that effort are a geographical and temporal description of the environmental conditions in Pearl Harbor, including Cu_{tot} and Cu_{diss} distributions, toxicity of copper to mussels and purple sea urchin, and WER calculations.

Table 1. Performance objectives for the demonstration of the integrated CH3D/seawater-BLM model in San Diego Bay, California, and Pearl Harbor, Hawaii.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met in San Diego Bay?	Actual Performance Objective Met in Pearl Harbor?
Quantitative	1. Comparison between modeled and measured Cu_{tot} concentrations	The model should explain ≥60% of the variance in the Cu_{tot} field data	Yes	Yes
	2. Comparison between modeled and measured Cu_{diss} concentrations	The model should explain ≥60% of the variance in the Cu_{diss} field data	Yes	Yes
	3. Comparison between modeled and measured Cu^{2+} concentrations	The model should predict values in the same order of magnitude as the Cu^{2+} field data	Yes	Not measured
	4. Comparison between modeled and measured toxicity	The model should predict the field data for toxicity within a factor of two	Yes	Yes
	5. Comparison between modeled measured WER	The model should predict the WER field data within a factor of two	Yes	Yes
Qualitative	1. Model stability	The integrated model should run 95% of the time with no interruptions	Yes	Yes
	2. Computational time	The integrated model should run ≥30% faster than running the CH3D and the seawater-BLM models alternatively	Yes	Yes

3.3 TEST SITE DESCRIPTION

San Diego Bay. San Diego Bay is an ideal site for the demonstration and validation of this model, as hydrological and chemical characteristics in the bay are at a relative steady state and well constrained. Hydrographic conditions in the bay indicate a minimal temporal change in salinity distributions, with predominantly hypersaline conditions in the back of the Bay (Chadwick and Largier, 1999a, 1999b; Blake et al., 2004). The quasi-steady-state hydrographic conditions in San Diego Bay are coupled with a long-term persistence of temporal and spatial distributions of total and dissolved copper concentrations that have been confirmed by a suite of studies (Zirino, Lieberman, and Clavell, 1978; Flegal and Sañudo-Wilhelmy, 1993; Esser and Volpe, 2002; Blake et al., 2004; Chadwick et al., 2004). Coupled to these relative constant conditions, there are no official wastewater point sources to the Bay, and the recognized point and non-point sources are well-studied (Johnson, Grovhoug, and Valkirs, 1998; Schiff and Diehl, 2002; Valkirs, Seligman, Haslbeck, and Caso, 2003; Schiff et al., 2004; Chadwick et al., 2004). The bay has been extensively studied for the fate and effects of copper as part of SERDP Projects CP-1156, CP-1157, and CP-1158. As a result of these studies, the information on sources, mass-balance, partitioning rates, and toxic effects is readily available (Blake et al., 2004; Chadwick et al., 2004; Shafer, Hoffman, Overdier, and Armstrong, 2004; Boyd et al., 2005: Rivera-Duarte et al., 2005; Rosen et al., 2005). A data gap for development of the seawater-BLM was the direct measurement of copper uptake by larvae of sensitive marine organisms, which was accomplished as part of this demonstration (Rosen et al., 2008).

The objective of this study was to demonstrate an integrated modeling system that provides an improved methodology for achieving compliance for copper in San Diego Bay, Pearl Harbor, and other DoD harbors in a manner consistent with the current regulatory framework recently released for copper in freshwater systems (U.S. EPA, 2007). And, while environmental characteristics make San Diego Bay an ideal place for the demonstration of the integrated modeling system, copper concentrations in the Bay reach values at or above the chronic WQC of 3.1 µg L^{-1} (Blake et al., 2004, Chadwick et al, 2004). These concentrations drive regulatory efforts on controlling the inputs of copper to the Bay. These efforts for point sources include TMDLs to address water quality impairment for Cu_{diss} in the Shelter Island Yacht Basin, a TMDL to control metal toxicity in stormwater from Chollas Creek, and the development of an NPDES to control copper sources from DoD ships.

The main source of copper to San Diego Bay is leaching from antifouling paint. Chadwick et al. (2004) updated the estimated copper inputs to San Diego Bay to a good degree of certainty. Their estimates are based on compilations of copper releases from civilian and Navy hull coating leacheates, civilian and Navy hull cleaning, other ship discharges (e.g., cooling water), point-source discharges, stormwater runoff, and atmospheric deposition (Johnson, Grovhoug, and Valkirs, 1998; PRC Environmental Management, Inc., 1997). These estimates were updated to account for recent improvements in estimates for various input rates and to incorporate estimates for Cu_{part} (Figure 4). Input rates were modified in response to the compilation of measurements from Seligman et al. (2001) and Valkirs et al. (2003). Following these measurements, the estimate for Navy hull coating leaching rates were updated to 3.8 µg cm^{-2} d^{-1}, and civilian and commercial hull leaching rates were updated to 8.2 µg cm^{-2} d^{-1} from the 17 µg cm^{-2} d^{-1} previously used for both of these releases (Johnson, Grovhoug, and Valkirs, 1998). The input of Cu_{diss} from civilian hull cleaning was updated based on a new discharge rate of 6-µg cm^{-2} $cleaning^{-1}$ reported by Schiff and Diehl (2002). Navy and civilian hull cleaning inputs for Cu_{part} were calculated from the dissolved estimates by applying the particulate to dissolved ratio reported by U.S. EPA (1999b). Atmospheric and direct rainfall inputs were calculated following PRC (1997), but were apportioned to surface area. Stormwater inputs of Cu_{diss} were updated to use measured event mean concentrations for all available watersheds with the

remaining areas calculated following the simple model method described by Johnson, Grovhoug, and Valkirs (1998). Cu_{part} loading from base flow and stormwater were calculated using the particulate: dissolved ratio for event mean concentrations reported by Woodward-Clyde (1996). The results of this analysis indicate Cu_{tot} loadings of about 20,400 kg y^{-1} and 22,000 kg y^{-1} for dry weather and wet weather conditions, respectively, and that releases from antifouling paint are the main source of copper, accounting for up to 65% within the bay (Chadwick et al., 2004; Figure 4). The analysis also indicates that the distribution of copper sources in the bay is localized, and mainly affected by the distribution of vessels. While the outer part of the bay (boxes 1 to 17) is dominated by pleasure boat sources, the inner part (boxes 18 to 27) is dominated by ship (i.e., commercial and military) sources.

Pearl Harbor. Pearl Harbor is located on the south-central side of the Island of Oahu. It is a large estuarine environment composed of three larger lochs (East, Middle, and West) and one smaller loch (Southeast) that are all separated by a narrow channel to the open ocean (Figure 5). The surrounding area is one of the most densely populated areas in the State of Hawaii. There are several highly urbanized streams that flow into Pearl Harbor, including the Halawa, Aiea, Kalauao, Waimalu, and Waimanu streams that empty into the East Loch, the Waiawa stream that empties into the Middle Loch, and the Kapahahi, Waikele, and Honouliuli streams that empty into the West Loch. The marine waters of Pearl Harbor are listed as impaired due to exceeding the water quality standards for nutrients, turbidity, suspended solids, and polychlorinated biphenyls (Hawaii State Department of Health, 2004). In contrast, Cu_{diss} concentrations in Pearl Harbor are low throughout most of the year, with an overall average plus or minus one standard deviation of 0.62 ±0.25 µg L^{-1} (Figure 6) (Earley et al., 2007). Although seasonal rain events can significantly affect these conditions, with the highest copper concentrations measured during a stormwater event in January 2006, toxicity was undetected in harbor samples (Earley et al., 2007). The demonstration in this system supports the validation of the integrated model for a range of natural conditions expected for marine harbors and embayments. The data from the Copper Water Compliance Studies at PHNS&IMF is available for this demonstration (Earley et al., 2007). The sampling and analysis plan for these studies included four sampling events covering the dry and wet seasons. The sampling parameters measured in ambient waters from Peal Harbor include hydrographic, chemical, and toxic characteristics that are essential for the development of WER and Translator studies. Therefore, while there may be some limited data collection requirements for this project, the majority of the calibration and validation data were provided by existing data sets, thus minimizing project costs.

As already explained, the objective was to demonstrate an integrated modeling system that will provide improved methodology for achieving copper compliance in DoD harbors. While environmental characteristics made Pearl Harbor an ideal place for this demonstration, copper concentrations in the harbor are below the WQC of 3.1 µg L^{-1} (Earley et al., 2007). Despite these low concentrations and the absence of toxicity, there are regulatory efforts on controlling the inputs of copper to the bay, mainly as a NPDES permit to discharges from the dry docks at the PHNS&IMF.

The main source of copper to Pearl Harbor is from ship discharges, and leaching from antifouling paint. Estimates of copper inputs to Pearl Harbor were updated from those from Johnson, Grovhoug, and Valkirs (1998), which are based on compilations of copper releases from civilian and Navy hull coating leacheates, civilian and Navy hull cleaning, other ship discharges (e.g., cooling water), point-source discharges, stormwater runoff, and atmospheric deposition (Johnson, Grovhoug, and Valkirs, 1998). The updated values account for recent improvements in measurements for various input rates (Figure 7). Input rates were modified in response to the compilation of measurements from Seligman et al. (2001) and Valkirs et al.

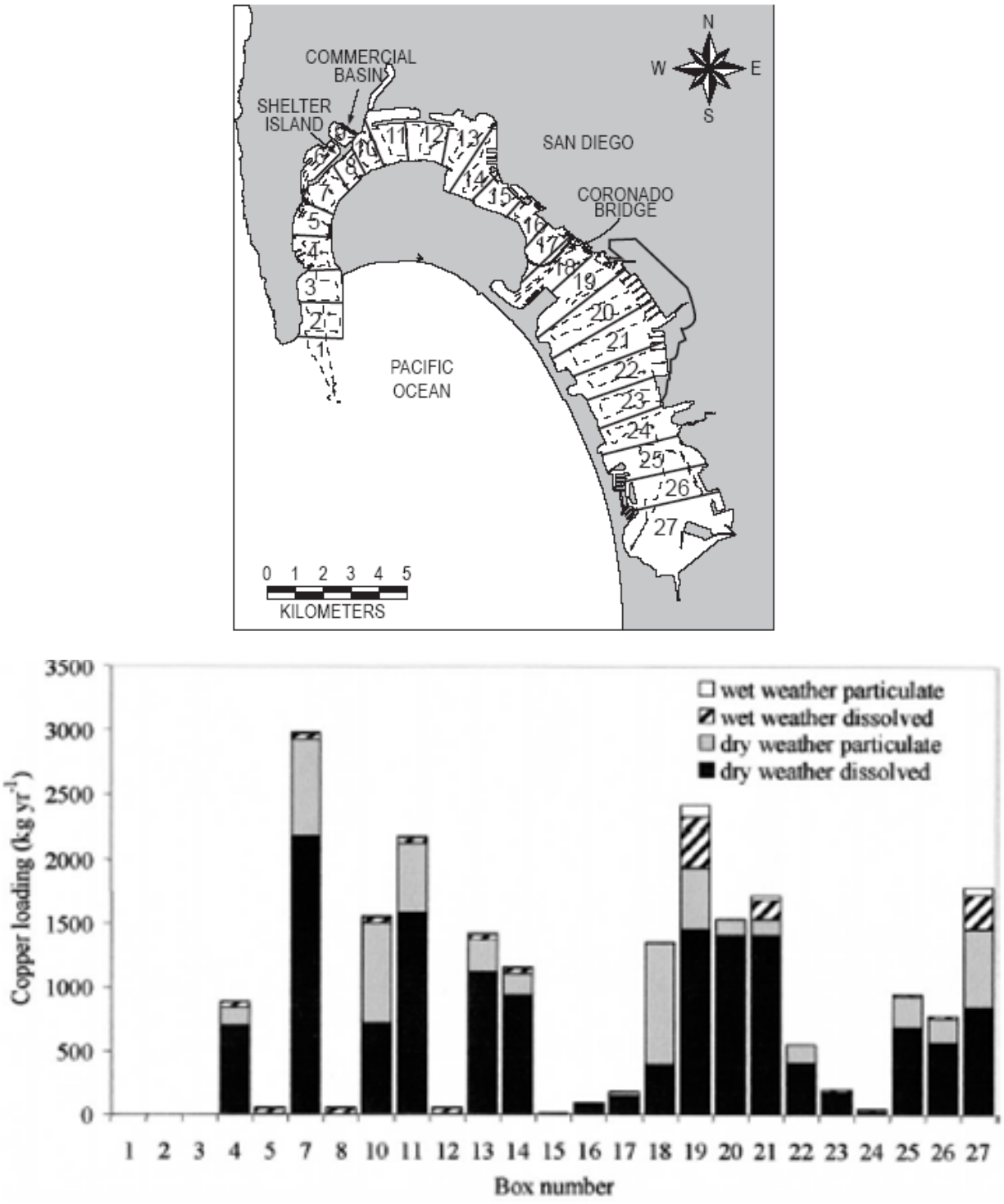


Figure 4. Estimated copper loading to the model regions designated by Chadwick et al. (2004). The top figure indicates the boxes within San Diego Bay and the transit path (broken lines) followed for sampling, and the figure at the bottom is the copper loading estimated at each box.

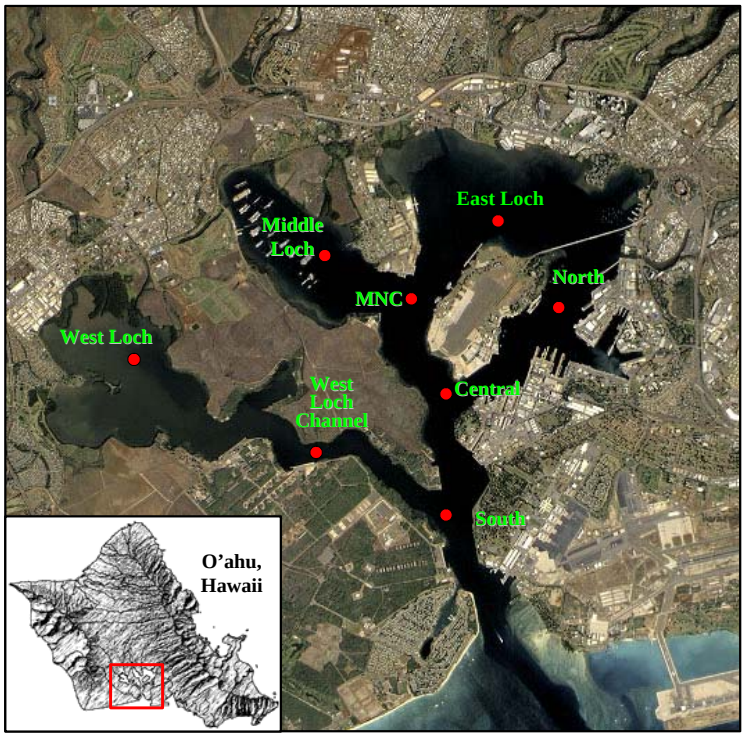


Figure 5. Picture of Pearl Harbor[4] with the sampling stations (red circles) used for the Copper Water Compliance Studies at PHNS&IMF (Earley et al., 2007). MNC is Station Middle North Channel.

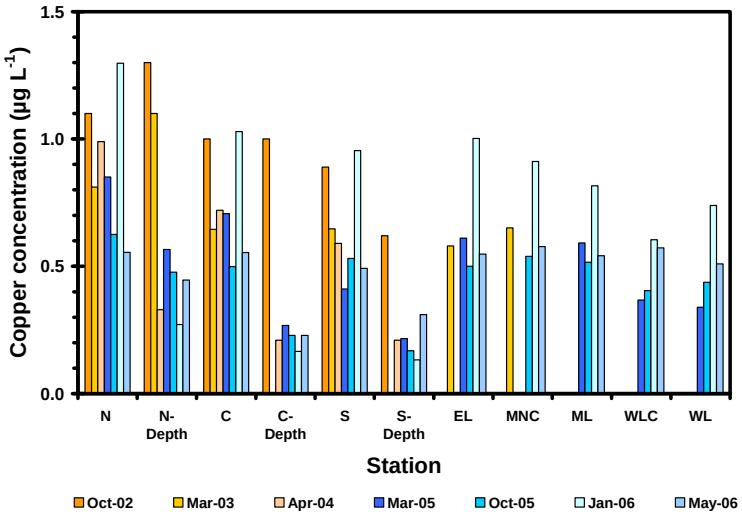


Figure 6. Seasonal dissolved copper concentrations (µg L^{-1} or ppb) throughout Pearl Harbor. Data from Earley et al. (2007).

[4] Picture modified from Wikipedia: http://en.wikipedia.org/wiki/Image:PearlHarbor_Sm.jpg

(2003). Following these measurements, the estimates for Navy hull coating leacheate were updated to 3.8 µg cm^{-2} d^{-1}, and civilian and commercial hull leacheate was updated to 8.2 µg cm^{-2} d^{-1} from the 17 µg cm^{-2} d^{-1} previously used for both of these releases (Johnson, Grovhoug, and Valkirs, 1998). On average, Cu_{tot} loading to Pearl Harbor is about 4561 kg yr^{-1}, of which ~74% is from Navy sources, ~18% from stormwater and watershed runoff, and ~6 % from sources related to civilian boats.

3.4 PRE-DEMONSTRATION TESTING AND ANALYSIS

Testing and analysis prior to the demonstration in San Diego Bay included the calibration of each of the F&T model CH3D, and the seawater-BLM, the integration of these two models, validation of the integrated model, and laboratory studies on copper bioaccumulation by larva of two sensitive organisms. CH3D and the seawater-BLM were calibrated with the data generated for San Diego Bay as part of the SERDP Project CP-1156. There were six sets of data, one for each of the six sampling campaigns done as part of the project. The dates for these campaigns were 30 August 2000, 30 January 2001, 11 May 2001, 19 September 2001, 27 February 2002, and 14 May 2002, and were designed as SD26, SD27, SD31, SD32, SD33, and SD35 by the SERDP CP-1156 project team. This designation is kept throughout the report and indicated as values in parenthesis. The sets of data from 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35) were used for the calibration of the models and the sets of data from 11 May 2001 (SD31) and 19 September 2001 (SD32) were used for the validation of the models.

Calibration of the BLM for seawater in San Diego Bay was done using the same data sets as for CH3D. Following the same approach, the same four sets of data were used for the calibration, and the other two sets of data were used for the verification of the seawater-BLM. As the BLM was initially developed for use in freshwater, calibration of the BLM for seawater also entails the modification of the program to represent the chemical speciation in seawater. Furthermore, bioaccumulation factors specific for copper-sensitive marine organisms are required for the development of the seawater-BLM. These bioaccumulation factors were evaluated with laboratory experiments. These experiments are described in Section 3.6, and were conducted with embryos of the bivalve Mediterranean mussel (*Mytilus galloprovincialis*) and the echinoderm purple sea urchin (*Strongylocentrotus purpuratus*) (Rosen et al., 2008).

Environmental characterization required for the demonstration in Pearl Harbor was done as part of a comprehensive study on copper regulatory strategies (Earley et al., 2007). This study included four sampling events conducted to characterize environmental conditions in the harbor during dry and wet seasons. The dates for these sampling events were 15–18 March 2005 (Event 1), 18–20 October 2005 (Event 2), 23–27 January 2006 (Event 3), and 15–19 May 2006 (Event 4). Events 1, 2, and 4 are for the dry season and 23–27 January 2006 (Event 3) is for the wet season. Samples from surface water (~ 1 meter deep) from the harbor were collected at eight locations (Figure 5). The parameters measured in these samples are those required for the implementation of the BLM, including total suspended solids (TSS), DOC, total organic carbon (TOC), Cu_{diss}, and Cu_{tot}.

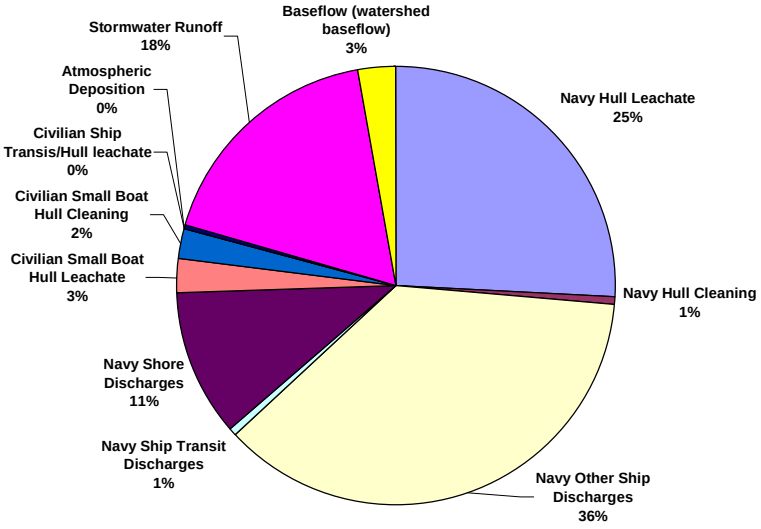


Figure 7. Estimated copper loading to Pearl Harbor updated by Earley et al. (2007) from Johnson, Grovhoug, and Valkirs (1998).

A different pre-demonstration strategy was used for each model for Pearl Harbor. Data from Events 1 and 4 were used for calibrating CH3D. The model parameters from these calibrations were applied for model validation with data from 18–20 October 2005 (Event 2). For the validation, the calibrated model parameters were upheld, and only the field data of TSS, DOC, and pH for 18–20 October 2005 (Event 2) were used. In contrast, there was no calibration of the seawater-BLM, which was validated with the data from the four cruises. As the two models were already integrated for the demonstration in San Diego Bay, the integrated CH3D/seawater-BLM model was used throughout the demonstration in Pearl Harbor. Copper bioaccumulation measured in San Diego Bay (Rosen et al., 2007) was used for this demonstration.

3.5 TESTING AND EVALUATION PLAN

3.5.1 Demonstration Installation and Start-Up

As explained above, the initial demonstration in San Diego Bay included preliminary calibration and validation of CH3D and seawater-BLM. It also included laboratory studies on copper accumulation by larvae of two sensitive organisms for the development of the seawater-BLM. Once these models were calibrated and validated, two consecutive approaches were followed for the integration of CH3D with the seawater-BLM. The first approach was through external integration, where the output of each model was used as feedback into the other model, with each model running separately. Once the external integration was validated, the two models were internally integrated into a unified model, with concurrent processing of data and output. This final integrated model was also calibrated and validated following the use of existing data as explained in Section 3.4 above. In the case of Pearl Harbor, the integrated model was used throughout the demonstration.

3.5.2 Period of Operation

The demonstration for San Diego Bay involved the preliminary and independent calibration and validation of both CH3D and the seawater-BLM, the integration of these models, and then the calibration and validation of the integrated model. A preliminary task for the demonstration was the

calibration of the seawater-BLM for marine species, which was conducted from March 2005 to November 2005. The demonstration started on March 2006, and the Technical Report was submitted in April 2007. The Demonstration for Pearl Harbor started in February 2007, and it concluded in April 2008. The schedule of tasks is shown in Figure 8.

3.5.3 Amount/Treatment Rate of Material to be Treated

No material was treated in this project.

3.5.4 Residuals Handling

There were no residuals from this project.

3.5.5 Operating Parameters for the Technology

Table 2 lists the operating parameters for the integrated model, including input, calibration, and validation parameters. For the F&T component, the input parameters included grid coordinates (x, y, and z), structural boundaries, bathymetry, water elevation and/or flow at the open boundaries, evaporation and heat transfer characteristics at the surface boundary, friction characteristics at the bottom boundary, particle concentration and size distribution within the model domain (or sources), copper concentration and fractionation at the open boundaries, and copper source location and strength within the domain and at the model boundaries. Primary calibration parameters for the F&T model included bottom friction coefficients, sub-grid scale dispersion coefficients, vertical turbulence parameters, copper-particle binding coefficients, and particle settling rates. Primary validation parameters for the F&T component included water elevation measurements, water velocity measurements, particle concentration and size distribution, and copper concentration and fractionation within the model domain.

Key calibration parameters for the seawater-BLM included the biotic-ligand binding constant estimated for the organism of interest, and the copper chemical speciation, copper species equilibrium constants, and chemical characteristics of the seawater. This speciation and characteristics of the seawater included Cu_{tot}, Cu_{diss}, Cu^{2+}, TOC, DOC, pH, alkalinity, salinity, and TSS. Validation parameters for the BLM included measured EC50, the tissue residue concentration that produces an effect in 50% of the population (ED50), WER, and Cu^{2+}.

The input parameters for the Integrated CH3D/seawater-BLM model are those for CH3D and seawater-BLM. The time-step and the spatial grid adjustments are the two main calibration parameters for the integrated model. However, an optimization of the efficiency of the Integrated CH3D/seawater-BLM model was performed part of the calibration. The validation parameters for the integrated model are comparisons with the results from CH3D and/or seawater-BLM, when these are run by themselves.

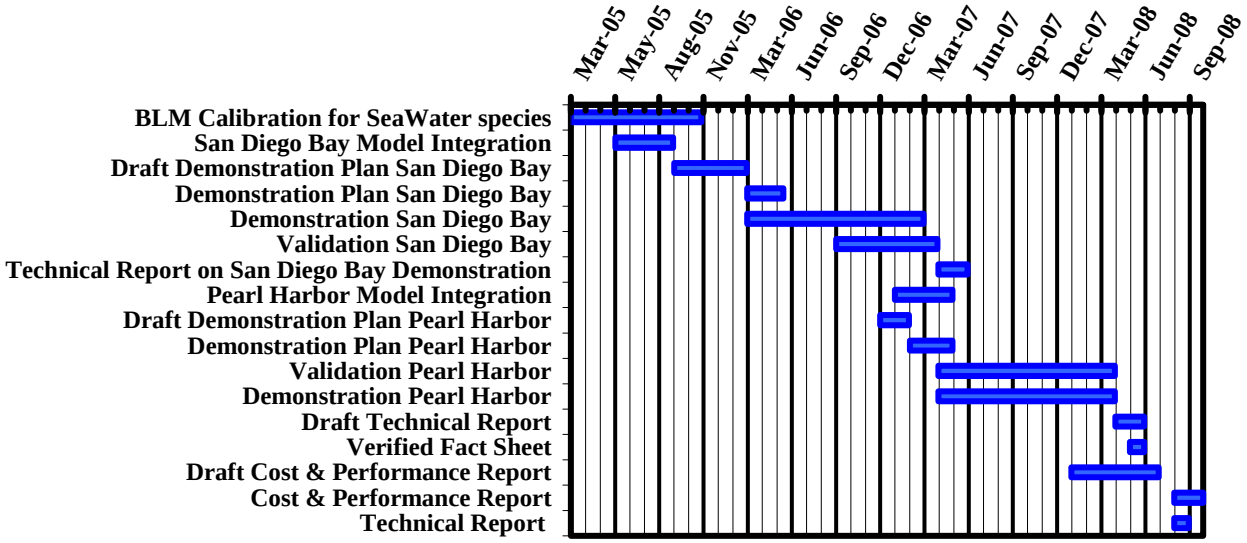


Figure 8. Schedule of tasks performed in the demonstration of the integrated model in San Diego Bay and Pearl Harbor.

The final integrated model provides information on the whole San Diego Bay or Pearl Harbor areas. As indicated in Section 3.4, the demonstration of the integrated model in San Diego Bay was performed with data generated under SERDP Project CP-1156, which encompass the whole area of San Diego Bay divided in 27 boxes (see map in Figure 4). Therefore, the integrated model provides information on toxic effects and WER calculations for the whole bay, with a resolution of 100 × 100 m within the bay. In contrast, the demonstration in Pearl Harbor was based on eight stations (Figure 5), with data from Earley et al. (2007), but the predictions by the integrated model are for the whole area within this harbor.

Table 2. Operating parameters for the CH3D and the seawater-BLM models.

Input Parameters	Calibration Parameters	Validation Parameters
CH3D Model		
Grid coordinates	Grid adjustments	Water surface elevation
Structural boundaries	Sub-grid scale dispersion coefficients	Water velocity
Bathymetry	Vertical turbulence	TSS distribution
Tidal height at boundaries	Copper binding coefficients	Cu_{tot} distribution
Evaporation	Particle settling rates	Cu_{diss} distribution
Sources location and strength	Tidal heights and phases at boundaries	Cu^{2+} distribution
Heat transfer		
Bottom friction coefficient		
TSS distribution		
Copper fractionation at boundaries		
Seawater-BLM		
Cu_{tot}	Biotic ligand binding constants	Copper toxicity, EC50
Cu_{diss}	Chemical equilibrium constants	Copper accumulation, ER50
TOC		WER
DOC		Cu^{2+}
TSS		
pH		
Temperature		
Salinity		
Alkalinity		
Integrated CH3D/seawater-BLM model		
Same as for both CH3D and seawater-BLM	Efficiency in comparison to running each model by themselves	Comparison to CH3D
	Time-step adjustments	Comparison to seawater-BLM
	Spatial grid size adjustment	

3.5.6 Experimental Design

The experimental design is depicted as the following data quality objectives.

Data Quality Objectives

Step 1. State the Problem:

Regulatory policy requires the development of site-specific WQS, TMDLs, and WERs. Empirical strategies for these requirements are expensive, time-consuming, fail to address the need for spatial and temporal resolution, and do not provide a predictive capability. An integrated numerical modeling capability is needed that will allow for the development of WQS, WERs, and TMDLs, as well as a management tool for the optimization of controls on copper inputs to the bay.

Step 2. Identify the decision:

a) What is an acceptable site-specific WQS for copper in San Diego Bay?

b) Based on this site-specific WQS, is copper being released to San Diego Bay at a rate that poses an unacceptable risk to the environment?

- If yes, what distribution and level of release would result in acceptable risk levels?
- If no, what is the additional capacity for release of copper in San Diego Bay?

Step 3. Identify the inputs to the decision:

a) The primary decision tool is the integrated CH3D/seawater-BLM model.

b) Data generated under the SERDP CP-1156 project were used for demonstration of the integrated model in San Diego Bay.

- The data for the campaigns of 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35) were used for the calibration of the models.
- The data for the campaigns of 11 May 2001 (SD31) and 19 September 2001 (SD32) were used for the validation of the models.

c) Data generated by Earley et al. (2007) were used for demonstration of the integrated model in Pearl Harbor.

- The data for the campaigns of 15–18 Mar 2005 (Event 1), 15-19 January 2006 (Event 3), and 15–19 May 2006 (Event 4) were used for the calibration of the integrated model.
- The data for the campaign of 18–20 October 2005 (Event 2) were used for the validation of the integrated model.

d) Bioaccumulation data from the ESTCP Project ER-0523 were used to calibrate the uptake parameters in the seawater-BLM.

e) Additional external data on partitioning, speciation, uptake and toxicity were used where appropriate for calibration and validation of the model.

Step 4. Define the Boundaries of the Study:

The boundaries of the study are governed by the model domain for the CH3D F&T model (Figure 1). The domain includes all of San Diego Bay and Pearl Harbor, and an offshore coastal zone that is included to provide adequate representation of the bay-ocean exchange.

Step 5. Develop a decision rule:

a) Integrated model WER: The integrated model was used to generate spatial distributions of the WER as a function of time. The magnitude of the WER was evaluated spatially and temporally to determine copper sensitive areas and conditions that could control the application of a site-specific WQS. If in general, the WER is greater than 1, then a site-specific WQS that is greater than the national ambient WQC would be appropriate for each harbor. If the WER less than 1, then a site-specific WQS that is less than the national ambient WQC would be appropriate. If the WER equals 1, then the current WQS is generally appropriate for each harbor.

b) Site-specific WQS: Based on the outcome of (a), then the integrated model should be used to recommend a site-specific WQS for each harbor. The WQS will address spatial and temporal variations in the WER. Different spatial and temporal zones may be considered in the WQS to address variations in binding characteristics within each harbor's water.

Step 6. Evaluate Decision Errors:

An erroneous assessment of the WQS could result in incorrect conclusions regarding risk to the environment, which in turn could lead to incorrect conclusions regarding the most optimal corrective action. These errors must be minimized by relying on multiple lines of evidence (model, data, literature) to characterize copper fate, transport and effects in each DoD harbor, and validation using independent lines of evidence (i.e., validation data sets).

Step 7. Optimize the Design for Obtaining Data:

Optimization of the study design consists of obtaining the required data of sufficient quality to implement, calibrate, validate, and execute the modeling program. As specified in Table 2 and Data Quality Objective 3, the key elements of this design include:

a) F&T Inputs: Develop sufficient data to define grid coordinates (x, y, and z), structural boundaries, bathymetry, tidal heights at the open boundaries, evaporation and heat transfer characteristics at the surface boundary, friction characteristics at the bottom boundary, particle concentration and size distribution within the model domain (or sources), copper concentration and fractionation at the open boundaries, and copper source location and strength within the domain and at the model boundaries.

b) F&T Calibration: Collect a minimum number of data sets with sufficient information to define the primary calibration parameters for CH3D including bottom friction coefficients, sub-grid scale dispersion coefficients, vertical turbulence parameters, copper-particle binding coefficients, particle settling rates, tidal heights and phases at model boundaries, and model grid adjustments.

Step 7. Optimize the Design for Obtaining Data (continued)

c) F&T Validation: Collect a minimum number of data sets with sufficient information to define the primary validation parameters for the F&T CH3D component, including water elevation measurements, water velocity measurements, particle concentration and size distribution, and copper concentration and fractionation within the model domain.

d) Seawater-BLM Inputs: Collect four data sets with sufficient data to define the input parameters for the seawater-BLM, including Cu_{tot}, Cu_{diss}, TOC, DOC, temperature, pH, TSS, alkalinity, and salinity. Salinity is used to define the concentration of major ions and carbonate in seawater.

e) Seawater-BLM Calibration: Collect historical information from scientific literature to define the primary parameters for calibration of the seawater-BLM, which include the biotic ligand binding constants and the equilibrium constants for the major chemical species in solution.

f) Seawater-BLM Validation: Collect a minimum number of data sets from each DoD harbor with information for the validation of the seawater-BLM, including site-specific toxicity and accumulation rates for the target species, empirically derived WERs, and measured Cu^{2+}.

3.5.7. Sampling Plan

As discussed in section 3.4 above, data developed from six sampling events as part of the SERDP Project CP-1156 were used for the demonstration in San Diego Bay, and from four sampling events by Earley et al. (2007) for the demonstration in Pearl Harbor. Only the samples from San Diego Bay for the studies on larval bioaccumulation of copper were collected as part of this project, as explained in Section 3.6 on the selection of analytical/testing methods. For San Diego Bay, the sampling plan for the six sampling events was developed based on modeling and environmental factors. Modeling factors include the partition of San Diego Bay into the 27 boxes described in the top map in Figure 4. The dimensions of each box were designed based on the modeling boundaries required for that project. Environmental factors affecting the sampling plan included the geographical distribution and seasonal variation of environmental parameters. Sampling included the whole extension of San Diego Bay to capture the complete extent of spatial variation. It also included the two main seasons observed, which are the dry season, which was characterized by higher salinities within the bay, and the wet season, with a decrease of salinity going into the head of the bay. For Pearl Harbor, the sampling plan for the four sampling events was developed to cover a minimum number of stations (i.e., eight) representative of the main bodies of water (i.e., lochs) within the harbor for regulatory purposes. As such, they do not represent an extensive study of the area, but do provide the general range for the environmental parameters within the harbor. The sampling included the two main seasons of dry and wet weather.

In San Diego Bay, some of the parameters were measured on transit, others were measured from subsamples, and others were measured by a combination of both approaches. For San Diego Bay, each sampling event consisted of transiting from the mouth to the head of the Bay in 1 day. The transect layout included two transverse legs within each of the 27 predefined sampling boxes (including two side basins) that are shown in the top map in Figure 4. During transit, continuous measurements and composite samples were collected with the Marine Environmental Survey Capability (MESC) real-time system, using a towed sensor package and a trace metal clean Teflon® seawater flow-through system. Sensors in the towed package included a conductivity, temperature, and depth (CTD) profiler outfitted with pH and dissolved oxygen (DO) sensors, a light transmissometer, and an ultraviolet (UV) fluorometer for hydrocarbon detection. The onboard

sensors included two fluorometers (UV and chlorophyll), two automated trace metal analyzers (TMA) for copper measurement, an acoustic Doppler current profiler (ADCP), a digital fathometer, a differential global positioning system (DGPS) navigation receiver, and a copper ion selective electrode (Cu-ISE). Vertical profiles were performed for every other box segment; otherwise, all sampling was performed at a depth of about 2 m.

Composite samples were collected from surface waters in San Diego Bay. These were collected from each of the box regions shown in the top map in Figure 4 by continuously pumping into pre-cleaned, 20-liter carboys. At the end of the transit through each box, subsamples were collected from the carboy for measurement of each of the parameters required.

All of the data from Pearl Harbor was measured from discrete samples. Samples of water were collected using a peristaltic pump and acid-cleaned polyethylene tubing at the desired depth in each station for each of the four sampling cruises. Due to access restrictions, and required overnight shipping of toxicity samples, the eight stations were sampled in two consecutive days, with four stations sampled each day. Discrete samples were collected for each of the measured parameters.

Analyses were performed for those environmental parameters that define physical, chemical, biological and toxicological characteristics of any coastal embayment. For San Diego Bay, these parameters include date, time, temperature, pH, light transmission, salinity, density, DO, Cu^{2+}, pH2 copper and zinc concentrations measured with the TMA, Cu_{tot}, Cu_{diss}, and zinc, TSS, bacterial production, DOC, alkalinity, total CO_2, chlorophyll, phaeopigments, bacterial abundance, cyanobacteria abundance, nitrates, phosphates, silicates, nitrites, ammonia, copper complexation capacity (Cu-CC), toxicity testing, and characteristics of organic ligands. Parameters measured in Pearl Harbor include date, time, temperature, pH, light transmission, salinity, DO, Cu_{tot}, Cu_{diss}, TSS, DOC, alkalinity, total CO_2, and Cu-CC. Analytical procedures include those described in Section 3.6, with the remaining procedures explained by Blake et al. (2004), Chadwick et al. (2004), Boyd et al. (2005), Rivera-Duarte and Zirino (2004), Rivera-Duarte et al. (2005), and Rosen et al. (2005, 2008).

3.5.8 Demobilization

Not applicable.

3.6 SELECTION OF ANALYTICAL/TESTING METHODS

An extensive suite of parameters was required for the characterization of a DoD harbor for determination of WER, TMDL, and for setting up a fate and effects and seawater-BLM model. However, among these parameters the following are the most relevant for the modeling: Cu_{tot}, Cu_{diss}, Cu^{2+}, TOC, DOC, TSS, salinity, alkalinity, and copper complexation capacity (Cu-CC), as well as toxicity testing. The preferred analytical methods for the measurement of these parameters are described below, as well as those for the parameters required to determine the copper accumulation by larvae of sensitive organisms.

In general, the fractionation of metals and organic matter between total and dissolved is achieved mechanically by a filtration through 0.45-µm, pore-size filters. This operational approach is accepted in most of the environmental sciences, and the only requirement is to state the size of the pores in the filter. The same approach was followed in SERDP project CP-1156 and by Earley et al. (2007). The main difference between Cu_{tot} and Cu_{diss}, as well as between TOC and DOC, is the filtration step.

Cu_{tot} and Cu_{diss}. Trace-metal clean techniques were used throughout sampling, handling, and analysis of the natural seawater samples (U.S. EPA, 1996b). Samples for Cu_{tot} and Cu_{diss} concentrations were collected in 1-L acid-cleaned, low-density polyethylene bottles. Cu_{tot} samples

did not require any treatment at sampling time, whereas Cu_{diss} samples were obtained with *in situ* filtration through 0.45-µm pore-size acid-cleaned, all-polypropylene cartridge filters. The samples were acidified to pH ≤2 with quartz still-grade nitric acid in a High Efficiency Particle Air (HEPA) class-100 all polypropylene working area. Following a 10-week period to allow for the oxidation of organic matter, the samples were concentrated according to the ammonium 1-pyrrolidine dithiocarbamate and diethylammonium diethyldithiocarbamate liquid-liquid procedure detailed by Bruland, Coale, and Mart (1985). The efficiency of the concentration procedure for copper was within 15% as determined with the standard reference materials (SRM), such as CASS-3 and/or CASS-4 of the National Research Council of Canada.

The concentration of copper in the pre-concentrates was measured by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) with stabilized platform techniques, Zeeman background correction, and following the method of standard additions. A coefficient of variation (CV) of ≤5% for replicate measurements was followed, as well as a recovery within 15% for direct injection of SRM 1643d of the National Institute of Standards & Technology. The method requires the extraction of procedural blanks of high-purity (18 MΩ cm^{-1}) water, which are used to define the method limit of detection, as three times the standard deviation of the procedural blanks.

Cu^{2+}. For San Diego Bay, this parameter was measured on transit and in the laboratory as part of the complexation titrations explained below. Cu^{2+} was not measured in Pearl Harbor. The main difference between these measurements is that, in general, on-transit measurements provide Cu^{2+} concentrations representative of natural seawater conditions, and the titration provides information on Cu^{2+} concentrations at relatively larger Cu_{tot} concentrations. Rivera-Duarte and Zirino (2004) detail the measurements of Cu^{2+}, however, only a brief description of the procedures is given. Measurements were done in a dark, class-100 working station, with constant stirring at 25 ±0.1°C. The activity (*a*) of Cu^{2+} was measured from the electrode potential (mV) between an Orion 94-29 copper ion selective electrode (Cu-ISE) and an Orion Ag/AgCl double-junction reference electrode. It is reported as $-\log a\,Cu^{2+}$, and termed pCu, which is equal to the concentrations of Cu^{2+} by assuming an activity coefficient of one. The electrodes were calibrated with seawater Cu-activity buffers made up of 2- × 10^{-4}-M Cu in filtered (0.45-µm) seawater with 1- ×10^{-3}-M of either ethylenediamine or glycine (Belli and Zirino, 1993; Zirino et al., 1998). The activity of Cu^{2+} in each buffer was calculated with a specific ion-interaction model for the concentrations of major ions (Belli and Zirino, 1993).

Cu-CC. Complexometric titrations were performed with seawater from San Diego Bay and Pearl Harbor. They are used for measuring Cu-CC, which is used in the calibration and validation of the seawater-BLM. As Cu-CC is related to the toxicity of the seawater (Rivera-Duarte et al., 2005), a brief description of its procedure is provided here. These complexometric titrations are used for the measurement of Cu-CC of the samples, which is the natural buffering capacity in the bay waters to sustain an input of copper without a specific adverse effect (i.e., EC50). The titrations involve the measurement of the potential (mV), using a Cu-ISE every time a small aliquot of copper titrant is added to the seawater. The titrations were done in a dark, class-100 working station, with constant stirring at 25 ±0.1°C. The potential (mV) was measured between an Orion 94-29 Cu-ISE and an Orion Ag/AgCl double-junction reference electrode. The electrodes were calibrated with seawater Cu-activity buffers as explained for Cu^{2+} above. Since the concentration of Cu^{2+} in each buffer was calculated with a specific ion-interaction model for the measured pH and the concentrations of major ions (Belli and Zirino, 1993), the calibrated response of the Cu-ISE is reported as the pCu (i.e., $-\log Cu^{2+}$) of the solution, assuming an activity coefficient of one. The titrations were performed with a TTT 85 Titrator and an ABU 80 Autoburette, both from Radiometer Copenhagen, connected to a

personal computer for continuous automatic recording of the data. First, the electrodes were calibrated and then allowed to equilibrate overnight in an aliquot of the seawater sample. The next day, an aliquot of 250–300 g of fresh seawater sample was weighed into a Teflon® beaker, and the electrodes were allowed to equilibrate in it for several minutes before starting the titration. Once the potential stabilized to within 0.1 mV sec^{-1}, the titration proceeded automatically by additions of 10 µL each and was completed after 99 mL of the titrant was added. The titrant was made with 200 µL of 1000 ±3 µg mL^{-1} High Purity Copper Standard added to 1 L of 18 MΩ cm^{-1} water containing 32-g NaCl. Cu-CC was estimated from the inflection point of the resulting titration curve using a MATLAB® routine (Rivera-Duarte and Zirino, 2004).

TOC and DOC. In San Diego Bay, sampled water was filtered through 0.7-µm nominal pore- size pre-combusted glass fiber filters for measurement of DOC. In Pearl Harbor, the water was filtered *in situ* through a 0.45-µm filter for DOC. For TOC and DOC, the samples were disposed into 5-mL amber ampoules containing 8-mL H_2PO_4. The ampoules were heat-sealed and stored frozen until analysis. Blanks of high-purity (18 MΩ cm^{-1}) water and method blanks (rinsed through syringe and filter unit) were included. TOC and DOC were measured with an MQ1001 high-temperature combustion total organic carbon analyzer (Qian and Mopper, 1996). Sodium phthalate was used to prepare standards that were run every 30 samples.

TSS. Approximately 1 L of seawater sample was sampled for TSS measurements. The analysis consisted in filtering approximately 900 mL through pre-dried and pre-weighed glass fiber filters (1.2-µm nominal pore size). Then the filters were rinsed with deionized water to remove dissolved salts, and dried and weighed to determine the mass of the filtered solids.

Salinity. Salinity was measured using a Seabird 19 CTD profiler. The CTD is part of the MESC system used to provide continuous, towed spatial mapping of water quality characteristics (Chadwick and Salazar, 1991). Based on the conductivity measurements from the CTD, salinity was calculated from the practical salinity scale (Lewis, 1980).

Alkalinity and Total CO2. Both total alkalinity and total CO2 were measured following the procedure of Hernandez-Ayon, Belli, and Zirino (1999). Approximately 30 mL of sample were introduced into a specially designed titration cell and were titrated with 0.1-M HCl. The titration was performed automatically by a computerized titration system and terminated after the second peak (bicarbonate) was clearly passed. The titration data were then processed with a MATLAB® program that calculated the difference derivative, performed a spline interpolation, filtered, and computed peak positions, and quantified both parameters.

Accumulation Studies. The only analytical methods that were required for the demonstration were those needed for the measurement of copper accumulation by larvae of sensitive organisms (Rosen et al., 2008). This testing included collection of seawater from areas representative of the range of conditions within San Diego Bay, exposure of embryos from sensitive organisms to a suite of copper concentrations in this seawater, recovery of the developed larvae, assessment of larval development success (i.e., toxicity), and measurement of copper concentrations in the larvae and in the exposure water. These tasks are explained in the following paragraphs.

Seawater from San Diego Bay. Surface seawater was collected from the mouth and the back of San Diego Bay (boxes 1 and 27 in San Diego Bay map, Figure 4) to represent the range of environmental conditions that could affect the copper toxicity of these waters to marine organisms. Trace metal clean techniques were followed throughout the collection of the waters. Acid-cleaned, high-density polyethylene tubing and Masterflex® tubing with a peristaltic pump were used for the collection. Seawater was filtered *in situ* to ≤0.45 µm, using acid-cleaned all-polypropylene cartridge filters. The typical volume of seawater required was from 30 to 70 L per site per organism tested.

Copper Accumulation Testing. Larval copper accumulation tests were performed following a modified version of the U.S. EPA method for estimating chronic toxicity to Pacific Coast marine and estuarine organisms (U.S. EPA, 1995). Embryos of a bivalve, the Mediterranean mussel (*M. galloprovincialis*), and an echinoderm, the purple sea urchin (*S. purpuratus*), were evaluated for normal larval shell development following exposures ranging from 48 hours (mussel) to 96 hours (sea urchin) (Figure 9). The purple sea urchins were collected from clean areas near the mouth of Mission Bay in San Diego, California, while mussels were acquired from Carlsbad Aquafarm, Carlsbad, California.

Gametes were obtained from the echinoderm by injection of 0.5-M KCl into the gonads of a number of individuals, while mussel spawning was induced by temperature shock. The number of individuals spawned was a function of the targeted larval density needed for the experiment. These targeted concentrations, determined by preliminary experiments, were a mussel embryo density of 60 embryos mL^{-1} for a total of 45,000 mussel embryos per replicate, and a target urchin embryo density of 40 embryos mL^{-1} for a total of 30,000 embryos per replicate. Within 4 hours of fertilization, the targeted embryo concentration was delivered to test beakers from an embryo suspension of known density.

The filtered water samples were spiked with copper 2 to 3 hours before the addition of the embryos. Seven copper concentrations were evaluated. On a nominal basis, these copper additions were 0, 2.9, 4.1, 5.8, 8.4, 12, and 17.2 µg L^{-1} for mussels, and 0, 5.8, 8.4, 12, 17.2, 24, and 35 µg L^{-1} for sea urchins. Each treatment had a total volume of 750 mL and was replicated three times. Tests were performed in seawater-soaked 1L high-density polypropylene containers and held in a temperature-controlled light chamber at 15°C with a 16-h light, 8-h dark photoperiod. Water quality (temperature, pH, DO, salinity) was monitored daily.

Larvae Filtration. The developed larvae were filtered upon verification that organisms in the control waters (i.e., no copper added) had reached the desired stage of development. After 72–96 h, sea urchin embryos achieving normal development are pyramidal in shape and have four well-developed skeletal rods (pluteus). Normally developed bivalve larvae possess a hinged D-shaped shell within 48 h (Figure 9). Once the development stage was achieved for the control seawaters, the samples were filtered through acid-cleaned 8-µm pore-size, 40-mm-diameter polycarbonate filters. The filtration and manipulation of samples was conducted in a HEPA class-100 trace-metal clean working area. After filtration, the filters were stored in 1.5-mL acid-cleaned polypropylene centrifuge tubes with caps for the subsequent digestion. The digestion was performed by pouring 100 µL of quartz still-grade nitric acid onto the filters in the centrifuge tubes, and allowing them to oxidize overnight. The following day, 1 mL of 18 MΩ cm^{-1} water was added to the centrifuge tubes, to reach a nitric acid concentration of about 1 N. The digestate was analyzed by dilution and direct injection into a GFAAS.

Prior to filtration, 5 mL of each replicate were subsampled and preserved in 10% buffered formalin. For each replicate, the first 100 larvae encountered at 40× magnification were scored as normal or abnormal. Following confirmation of normal distribution and equality of variances with arc-sine, square root transformed data, the proportion of normal larvae was used to compute EC50 values using Probit analyses with ToxCalc™ software (Tidepool Scientific Software, ToxCalc™ 2002). http://www.members.aol.com/tidesoft/toxcalc/.

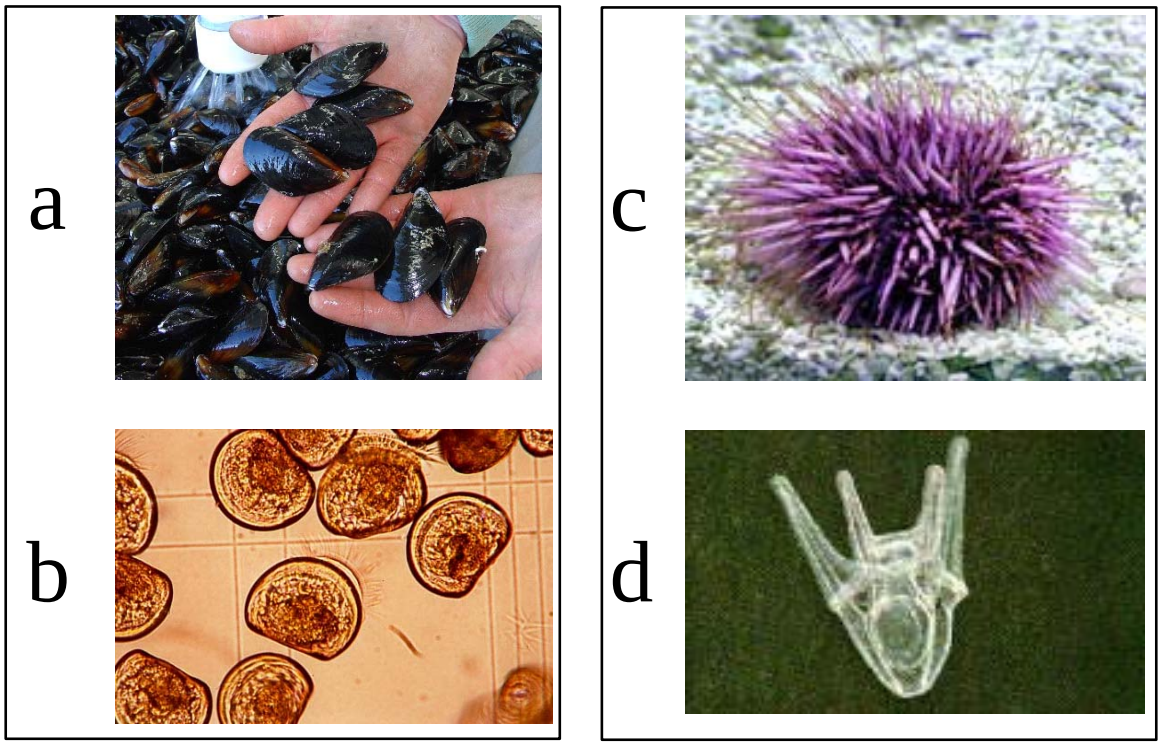


Figure 9. Test organisms used in this study include (a) Mediterranean mussels (*Mytilus galloprovincialis*; adults, 5 to 7 cm), (b) Mediterranean mussel D-shaped larvae (120 µm), (c) purple sea urchin (*Strongylocentrotus purpuratus*; adults, 5- to 7-cm diameter), (d) sea urchin pluteus larva (200 µm).

Copper Concentration for Accumulation Studies. Copper concentrations used for EC50 and ED50 calculations were based on Cu_{diss} measured by direct-injection GFAAS values obtained for each exposure concentration. Concentrations in three different types of samples were measured. These include the filter plus larvae digestate, the filtered seawater spiked with copper, and the original filtered seawater concentration at each of the sites. Trace-metal clean techniques were used throughout the sampling, handling, and analysis of the samples. As indicated above, the copper concentration in the digestates was measured by dilution and direct injection into a GFAAS with stabilized platform techniques, Zeeman background correction, and the method of standard additions. The CV of replicate measurements was less than or equal to 5.0%. The method limit of detection is defined as three times the standard deviation of the procedural blanks. Samples for filtered (i.e., dissolved) copper concentrations were collected into 15-mL acid-cleaned, low-density polyethylene bottles and were acidified to pH less than or equal to 2, with quartz still-grade nitric acid in a class-100 all-polypropylene working area, and were analyzed by dilution and direct injection into a GFAAS. The 1-L samples were collected from the original seawater for each site. The samples were collected into HDPE acid-cleaned bottles, and 2 mL of quartz still-grade nitric acid were added to each sample. Approximately 10 weeks were allowed for the oxidation of organic matter, and then the samples were concentrated following the APDC/DDDC liquid/liquid procedure detailed by Bruland, Coale, and Mart (1985). The copper concentration in the pre-concentrates was also measured by dilution and direct injection into a GFAAS.

3.7 SELECTION OF ANALYTICAL/TESTING LABORATORY

An in-depth knowledge of the capabilities of any laboratory is required for analysis of environmental samples to appropriate levels. The analytical laboratory must meet the performance criteria explained in the previous section. There are commercial analytical laboratories that can measure the parameters needed to the precision required for environmental analysis and meet the above performance criteria. However, these laboratories were not required for the demonstration, as the data are readily available from SERDP Project CP-1156.

The only analytical testing performed for the demonstration was that required for the measurement of copper accumulation by larvae of sensitive organisms. These organisms are the Mediterranean mussel (*M. galloprovincialis*) and the purple sea urchin (*S. purpuratus*). These measurements were performed at the laboratories at SSC Pacific, and include induction of spawning by adult organisms, toxicity testing, and measurement of Cu_{diss} in larvae and seawater samples.

Private analytical laboratories that could have been selected for this project include the following:

- Battelle Sequim Operations, Pacific Northwest National Laboratory, 1529 W. Sequim Bay Rd., Sequim, WA 98382, voice (360) 681-3627, fax (360) 681-3699.
- Applied Marine Sciences, Inc., 502 N. Highway 3, Suite B, League City, TX 77573, voice (281) 554-7272, fax (281) 554-6356.
- Columbia Analytical Systems, Inc., 1317 South 13th Avenue, Kelso, WA 98626, voice (360) 501-3316, fax (360) 636-1068.

4. PERFORMANCE ASSESSMENT

4.1 PERFORMANCE CRITERIA

The performance of the integrated model was assessed following the criteria shown in Table 3.

Table 3. Performance criteria.

Performance Criteria	Description	Primary or Secondary
Reliability of CH3D model prediction	Comparison of measured and CH3D-modeled distributions of Cu_{tot}	Primary
Reliability of CH3D model prediction	Comparison of measured and CH3D-modeled distributions of Cu_{diss}	Primary
Reliability of seawater-BLM prediction	Comparison of measured and seawater-BLM modeled distributions of Cu^{2+}	Primary
Reliability of seawater-BLM	Comparison of measured and seawater-BLM modeled distributions of copper toxicity	Primary
Reliability of integrated model	Comparison of field data with modeled distributions of copper toxicity and WER	Primary
Predictive capability of integrated model	Evaluation of model stability	Secondary
Predictive capability of integrated model	Evaluation of computational time	Secondary

4.2 PERFORMANCE CONFIRMATION METHODS

The performance of the integrated model was assessed following the criteria shown in Table 4. The primary criteria follow that described by the performance criteria (Table 3). Our personnel evaluated the secondary criteria from observations. The integrated CH3D/seawater-BLM model runs with no stability problems and is 100% stable. The improvement in running time from the external to the internal mode is obvious. In external mode, once the CH3D finishes a run, the data are processed and provided to the seawater-BLM. This process takes from 2 to 3 days. In the internal mode, the data are transferred automatically from the CH3D to the seawater-BLM in a matter of seconds. However, the time for running each independent model remains the same in either mode.

Table 4. Performance criteria and confirmation methods for the demonstration.

Performance Criteria	Expected Performance (Pre-Demo)	Performance Confirmation Method	San Diego Bay Actual (Post-Demo)	Pearl Harbor Actual (Post-Demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)				
PRIMARY CRITERIA (Performance Objectives) (Quantitative)				
Reliability of CH3D Model prediction	The model should explain ≥60% of the variance in the field data for Cu_{tot}	Comparison of measured and modeled Cu_{tot} distributions	Yes, explain 74% to 93% of variance	Yes, explain 61% to 94% of variance
Reliability of CH3D Model prediction	The model should explain ≥60% of the variance in the field data for Cu_{diss}	Comparison of measured and modeled Cu_{diss} distributions	Yes, explain 68% to 92% of variance	Yes, explain 68% to 92% of variance (when $\Delta C > 0.22$ µg L^{-1})
Reliability of seawater-BLM prediction	The model should predict values in the same order of magnitude as the field data for Cu^{2+}	Comparison of measured and predicted Cu^{2+} values	Yes, 97% are within an order of magnitude	No, there are no available *in situ* Cu^{2+} measurements
Reliability of seawater-BLM	The model should predict the field data for toxicity within a factor of two	Comparison of measured and modeled copper toxicity distributions	Yes, for 87% or better of the predicted values	Yes, for 83% or better of the predicted values
Reliability of Integrated model	The model should predict the field data for WER within a factor of two	Comparison of field data with modeled WER distributions	Yes, 80% are within this range	Yes, 98% are within this range
SECONDARY CRITERIA (Performance Objectives) (Qualitative)				
Stability of Integrated model	Integrated model should be 100% stable	Stability of integrated model to complete repetitive runs	Yes, model is 100% stable	Yes, model is 100% stable
Time optimization of Integrated model	Integrated model should be 30% faster than parallel running of models	Measurement and optimization of time for computation	Yes, faster by up to 3 days	Yes, faster by up to 3 days

4.3 DATA ANALYSIS, INTERPRETATION, AND EVALUATION

The calibration and validation of the CH3D, seawater-BLM, and the integrated models were done by comparison with field data generated in previous efforts. This task was accomplished with scatter plots, having the measured field data plotted as independent variable in the abscissa (x-axis), and the modeled data plotted as dependent variably in the ordinate (y-axis; U.S. EPA, 2006). These plots were used to evaluate the degree of correlation between the model predictions and the actual data, and to estimate the percentage of the variability of the field data that could be explained by the model.

Field-developed WER is the alternative existing process, which includes sampling, measurement of quality parameters, and testing of toxicity. As indicated above, the field data were already available for this site, as well as a WER for San Diego Bay (Rosen et al., 2005).

4.3 1 Copper Accumulation by Sensitive Organisms

To support the development of the copper seawater-BLM, a series of laboratory bioaccumulation exposures with embryos of bay mussel (*M. galloprovincialis*) and purple sea urchin (*S. purpuratus*) were performed (Rosen et al., 2008). These experiments were done to determine the tissue Cu concentration(s) at which toxicity occurs, using natural surface waters collected from San Diego Bay. The larval tissue concentrations were measured following exposures lasting 48 h for mussel or 96 h for sea urchins, the approximate time required for each organism to reach the D-shaped and pluteus larval stages, respectively. Tissue concentrations were then related to any observed effects on larval development for each of seven concentrations of copper added to seawater. EC50 values were predicted to vary depending on water chemistry characteristics of the samples (e.g. DOC), while the ED50 (tissue concentration resulting in 50% abnormally developed larvae) were predicted to remain relatively constant. This hypothesis is based on critical body residue (CBR) theory, which suggests that a predictable critical tissue concentration will result in toxicity (McCarty and Mackay, 1993).

Table 5 lists water quality characteristics associated with five different samples employed in the copper accumulation studies. While most parameters were quite similar, DOC and Cu_{diss} concentrations were always larger in South Bay samples compared to concurrently tested North Bay samples. Toxicity metrics based on water concentration (e.g., EC50) and tissue concentrations (e.g., ED50) from four mussel and two sea urchin exposures are shown in Table 6. Mussel EC50 values were positively correlated with DOC concentration ($r^2 = 0.995$; $p = 0.0475$) with exclusion of the North 3 sample. Overall, EC50s differed by a factor of 2 for mussel larvae and a factor of 1.4 for sea urchin larvae, among samples over space (North and South Bays) and time (up to three different sampling events, depending on species). These findings substantiate previous work that illustrated both a link between EC50 and DOC (Arnold, 2005; Rosen et al., 2005; Arnold, Cotsifas, and Corneillie, 2006), as well as temporal and spatial variability in the potential for copper toxicity in San Diego Bay when toxicity is expressed using exposure water concentrations (Blake et al., 2004; Rosen et al., 2005; Rivera-Duarte et al., 2005). Although differences among EC50 values are not as great as one might expect in other water bodies where DOC concentration varies to a greater degree (Arnold, Cotsifas, and Corneillie, 2006), confidence intervals around the EC50 values generally did not overlap, and the coefficient of variation (CV) among EC50s was relatively large (28.5 and 25.5% for *M. galloprovincialis* and *S. purpuratus*, respectively).

Table 5. Water quality measurements (mean ±1 sd) from controls (e.g., no added Cu) during each of three larval toxicity and bioaccumulation experiments conducted with surface water from San Diego Bay, California.

Sample ID	Exp. No.	pH	DO (mg L^{-1})	T°C	Salinity	DOC (mg L^{-1})	Cu_{diss} (µg L^{-1})
North	1	7.89 ±0.08	8.65 ±0.98	15.5 ±0.11	34.3 ±0.16	1.30	0.90
North	2	7.85 ±0.19	7.28 ±0.26	15.3 ±0.21	34.1 ±0.16	1.70	0.60
South	2	8.01 ±0.19	7.38 ±0.47	14.8 ±0.10	35.8 ±0.08	2.24	2.50
North	3	8.09 ±0.02	7.97 ±0.06	15.8 ±0.32	34.2 ±0.10	2.47	0.90
South	3	8.20 ±0.02	7.97 ±0.03	16.0 ±0.29	35.4 ±0.13	3.43	2.50

Whole-body ED50s averaged 48.9 and 142 µg g-dw^{-1} for *M. galloprovincialis* and *S. purpuratus* larvae, respectively (Table 6). Unlike EC50s, whole-body ED50s varied little among experiments, as indicated by very low CVs (7.9 and 11.0% for *M. galloprovincialis* and *S. purpuratus*, respectively) and overlapping confidence intervals (Table 6), suggesting that whole-body residues were a better predictor of toxicity than exposure water concentration. Graphical representations of the dose-responses for copper based on water and whole-body tissue concentrations (Figure 10) strengthen this conclusion.

ED50 values were similar to the few literature values reported for similar species and life stages. A whole-body copper ED50 of 114 µg g-dw^{-1} was calculated from data reported by Radenac, Fichet, and Miramand (2001) for comparable exposures with embryos of the European sea urchin (*Paracentrotus lividus*). This calculation is particularly interesting because *P. lividus* appears to be as much as six times less sensitive to copper than *S. purpuratus*, based on the reported EC50 (115 µg L^{-1}) (His et al., 1999) of the former. This result is expected, as tissue measurements consider only the fraction of copper available for uptake, while dissolved water concentrations, which do not differentiate between free and complexed metal, do not.

Although some difference in sensitivity was apparent between the two species evaluated in this study when data were expressed in terms of CBRs (ED50s varied by a factor of nearly three), note that no-observable-effect doses (NOEDs) were identical (both averaging 23.3 µg g-dw^{-1}) for both species. In addition, digestion of the calcareous structures (e.g., larval shell for mussels and skeletal rods for sea urchin pluteus) prior to acid digestion of tissues in an effort to calculate soft tissue residues, reduced the difference in ED50s between species to less than a factor of 2 (Rosen et al., 2008). Therefore, CBR theory appears to apply for these species, with a predictable and similar response to specific copper concentrations accumulated by both *M. galloprovincialis* and *S. purpuratus* larvae.

Observed differences in ED50s, however, are not surprising, as both accumulation rate and compartmentalization of metals following uptake is known to differ among organisms. Bioconcentration factors were higher for mussel larvae than sea urchin larvae in similar exposures (Rosen et al., 2008), suggesting a higher rate of uptake by the mussels. In addition, inorganic granules (McGeer et al., 2003; Vijver et al., 2004) and metallothionein-like proteins (Widdows and Donkin, 1992; Roesijadi et al., 1997; McGeer et al., 2003; Vijver et al., 2004) allow many aquatic organisms to sequester, store, and detoxify high concentrations of metal without impact. Metallothioneins have been measured at elevated levels in mussel (Roesijadi, Hansen, and Unger, 1997; Geffard, Geffard, His, and Amiard, 2002b), oyster (Geffard, Budzinski, and His, 2002a; Damiens et al., 2006) and sea urchin (Nemer, Travaglini, Rondinelli, and D'Alonzo, 1984) larvae following metal exposure originating with embryos. It is feasible that *S. purpuratus* larvae possess a better ability to induce these processes than *M. galloprovincialis*, providing greater tolerance to elevated concentrations. Regardless, for both species, the repeatability of observed effects at specific whole-body concentrations suggests that tissue concentrations are very good surrogates for the fraction of copper that is biologically available and actually reaches sites of toxic action for these particular endpoints.

Table 6. Copper toxicity metrics based on exposure water concentrations (EC50) and whole-body residues (ED50) from copper-spiked seawater samples collected from North and South San Diego Bay, California.[5]

		Water concentration (µg L^{-1})				Whole-body residue (µg g-dw^{-1})			
Organism	Sample ID	Exp. No	NOEC	LOEC	EC50 (95% CL)	Controls (mean ± sd)	NOED	LOED	ED50 (95% CL)
Mussel	North	1	4.10	5.40	6.36 (6.22–6.49)	5.84 ± 4.20	18.4	38.2	50.3 (48.4–52.2)
	North	2	5.34	7.78	8.68 (8.47–8.89)	2.29 ± 0.60	24.0	31.6	44.0 (36.9–52.7)
	North	3	6.87	13.4	9.64 (9.60– .68)	5.69 ± 3.49	31.7	75.4	47.7 (46.9–48.5)
	South	2	7.08	9.89	12.8 (12.6– 3.0)	9.65 ± 0.00	19.3	24.0	53.4 (50.8–56.0)
Sea Urchin	North	3	9.1	12.7	14.3 (13.8–14.9)	3.68 ± 3.95	22.9	67.2	131 (108–155)
	South	3	14.1	16.5	20.6 (20.3–21.0)	3.57 ± 0.83	23.8	65.7	153 (115–192)

[5] Toxicity endpoints were normal embryo-larval development of the Mediterranean mussel (*M. galloprovincialis*) or purple sea urchin (*S. purpuratus*). Metrics include the no-observable-effect concentration (NOEC) and dose (NOED), lowest-observable-effect concentration (LOEC) and dose (LOED), and median effects concentration (EC50) and dose (ED50). CL = confidence limit.

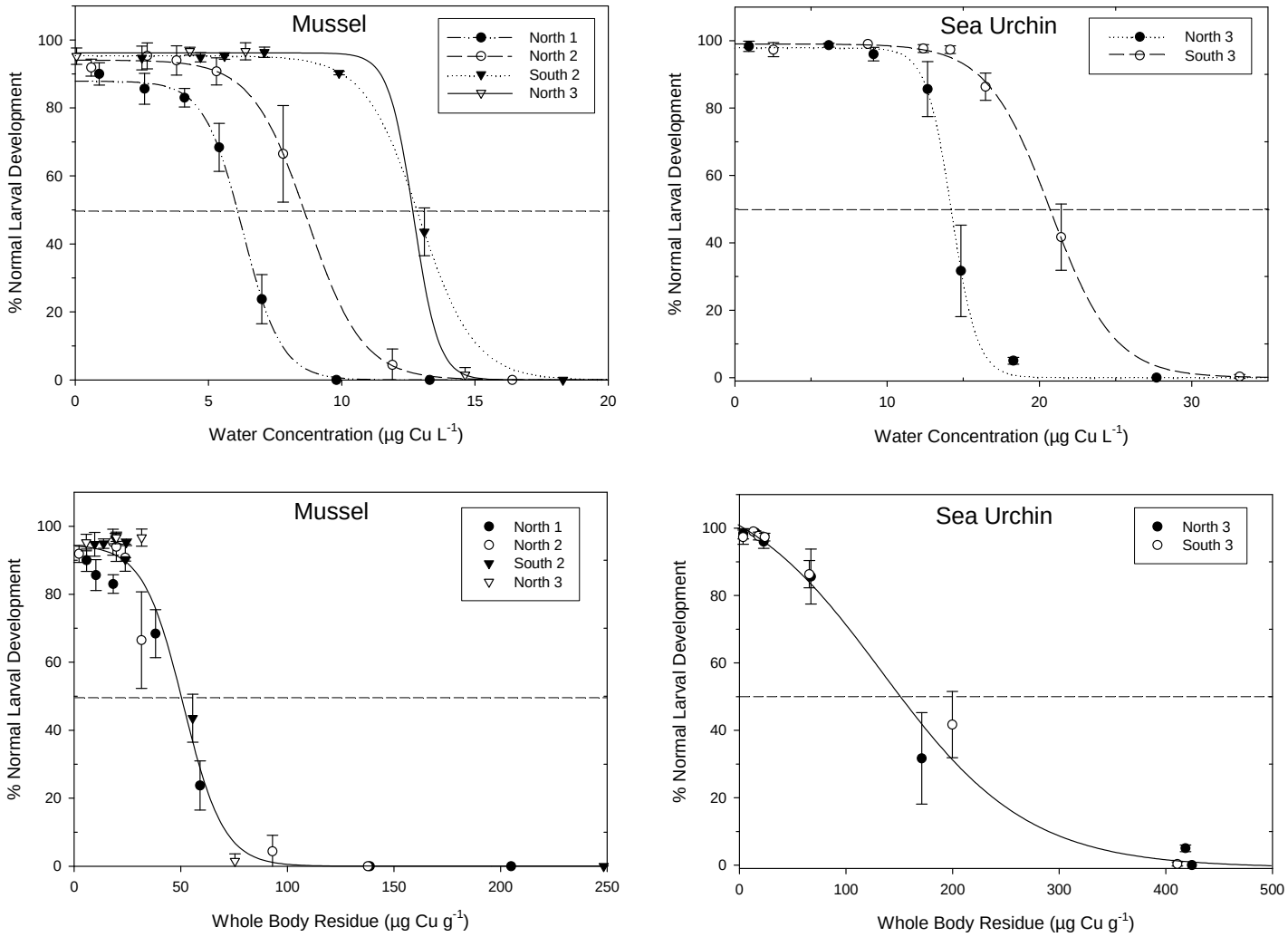


Figure 10. Copper dose responses from embryo-larval development tests with mussels (*M. galloprovincialis*) and purple sea urchins (*S. purpuratus*) expressed as water concentration or whole-body residues (from Rosen et al., 2008). Intersection between fitted curves and dotted lines indicate approximate median effect concentration or dose (whole-body concentration).

The copper ED50 data developed by this study for *M. galloprovincialis* and *S. purpuratus* larvae are considerably higher than the median lethal accumulation (LA50) values developed by MacRae et al. (1999) for rainbow trout (1.4 µg g-ww^{-1} or 10 nmol Cu g-ww^{-1}) which were used for calibration of the freshwater-BLM (Di Toro et al., 2001). A few factors may explain this apparent discrepancy. First, it is well known that the bioconcentration of metals can vary greatly with the species of organism (Luoma and Rainbow, 2005). Invertebrate zooplankton is known to accumulate metals to particularly high levels (Horowitz and Presley, 1977; Fowler, 1986; Rainbow and White, 1990). Fish, however, closely regulate internal concentrations, and therefore, typically possess lower concentrations than invertebrate zooplankton populations (Horowitz and Presley, 1977; Fowler, 1986).

Perhaps more importantly, however, is that the critical concentrations reported from this study are based on whole-body residues, while the fish LA50 is based on accumulation at the specific site of toxic action, the gill. Therefore, until the site of toxic action is determined and measured in *M. galloprovincialis* and *S. purpuratus* larvae, meaningful comparisons are difficult.

Another point to consider is that whole organ (e.g., the gill) or whole-body accumulation levels do not necessarily equate to accumulation at the immediate site of action of toxicity (e.g., a sensitive enzyme system). The fact that whole-body accumulation levels can be correlated to effects may be related to there being an underlying covariation between whole-body and enzyme-specific accumulation levels. To the degree that this is the case, organism-specific differences in how Cu is accumulated at physiologically inert binding sites (i.e., sites other than the biotic ligand) could contribute to the differences in apparent whole-body LA50 values that have been reported for different organisms. Thus, caution should be exercised with regard to inferences that are drawn from comparisons of measured LA50s for different organism types.

4.3.2 Seawater-BLM

The application of the freshwater-BLM to seawater requires formulation of a valid chemical model. As explained in section 2.1 above, the BLM was developed for freshwater conditions, and in that formulation, it does not adequately describe the chemical speciation under seawater conditions. A schematic representation of the differences between freshwater and seawater chemical conditions is shown in Figure 2. Direct application of the freshwater-BLM to conditions in San Diego Bay to replicate the results from the combination of *in situ* measured Cu^{2+} and laboratory complexometric copper titrations performed for SERDP project CP-1156 are indicative of the required modifications to the freshwater-BLM to perform in seawater. Comparison of the speciation predictions with the combined measured results indicate that the freshwater-BLM over-predicts Cu^{2+} concentrations by up to two orders of magnitude and that the BLM-predicted response (i.e., slope) to copper additions differs from the observed titration results (Figure 11). Possible causes for these differences include probable differences between terrestrial and marine NOM, chemical changes in NOM in saline environments, inadequacy of ion activity corrections for saline environment, and proton (H^+) interactions with DOM.

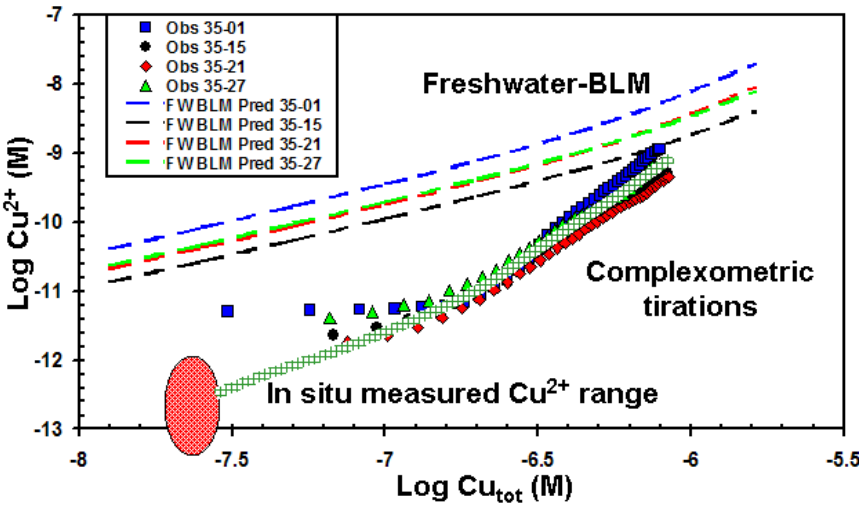


Figure 11. Comparison of freshwater-BLM predictions to *in situ* measured and copper complexometric titrations in waters of San Diego Bay. The green shaded area depicts the expected response of Cu^{2+} with increasing Cu_{tot} in ambient waters. Symbols show measured data and lines indicate modeled results.

4.3.3 A Calibration of Seawater-BLM San Diego Bay

Combination of the data from *in situ* measured and complexometric titrations provides a thorough description of the response of Cu^{2+} with increases of Cu_{tot} in seawater. Preliminary testing indicated that the value for L1 estimated from the complexometric titrations alone does not represent the stronger characteristics indicated by *in situ* measurements. As the titrations are done in batches in aliquots kept in a Teflon® beaker, with continuous automatic additions of copper (Rivera-Duarte and Zirino, 2004), the initial Cu^{2+} is compromised. This conclusion is evident from the initial Cu^{2+} concentrations measured in the titrations in comparison to those measured *in situ* with a flow-through system during the sampling transects. The *in situ* flow-through system provides a lower initial Cu^{2+} because the thin layer, in contact with the electrode membrane, is continuously replenished with fresh seawater, avoiding the increment in copper concentration as it leaches from the membrane (Zirino, DeMarco, Rivera-Duarte, and Peccic, 2002). This *in situ* measured Cu^{2+} concentration is assumed as representative of natural conditions in the bay.

The seawater-BLM modified as explained above was calibrated with data from cruises of 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35). As explained above, calibration for marine NOM was performed by analyzing the combination of *in situ* measured Cu^{2+} with copper complexometric titrations for San Diego Bay. The data were analyzed by affinity distribution to characterize the number, concentration, and strength of hypothetical binding sites required to model them. A three-site DOC model was fit to the data using the software PEST (Watermark Numerical Computing, http://www.grac.org/ pest.html) to optimize binding constants and site densities. Data from three titrations showed much higher Cu^{2+} than the bulk of the data, and were excluded from the calibration process. Additionally, in each titration dataset, data that showed an unreasonable response between Cu^{2+} and Cu_{tot} were excluded. Specifically, consecutive observations that showed a slope for log Cu^{2+} vs. log Cu_{tot} that was less than unity were excluded. All excluded data can be identified in Figure 12, which includes information from two published studies on the response of Cu^{2+} to increases in Cu_{tot} in seawater (Kogut and Voelker, 2001; Buck and Bruland, 2005). The initial lower values shown for the titrations are the Cu^{2+}

concentrations measured *in situ* with the flow-through system during transit, and the rest of the data were measured in laboratory-controlled complexometric titrations. These visual comparisons show the capacity of the seawater-BLM to predict these lower *in situ* Cu^{2+} concentrations, as well as the Cu^{2+} measured in the titrations at relatively high Cu_{tot} concentrations.

Consistency between the set of titrations analyzed was reasonable, with three binding sites appearing to be present over the range of copper concentrations tested, with apparent Log K values that range from strong (Log K 9.14) to very strong (Log K 12.9) binding strength. The apparent binding site concentrations were inversely proportional to binding strength, as expected, with a range of 33 to 878 nmol mg C^{-1} (Table 7). Inclusion of a fourth site did not improve model fit. The binding site concentrations are expressed per milligram of carbon, since the abundance of these binding sites is assumed to fluctuate in accordance to the concentration of DOC.

Table 7. Binding characteristics for the three (L1, L2, and L3) hypothetical binding sites characterized from the combination of *in situ* measurements and copper complexometric titrations in waters from San Diego Bay.

	L1	L2	L3
Log K	12.9	11.0	9.14
[L] (nmole mgC^{-1})	33.5	127	878

Optimized binding constants are similar to literature values for marine DOC. Previously published parameter values that describe the interaction between copper and the strongest organic ligand vary widely (e.g. Log K values range from 10.8 to 16.1, and ligand concentrations range from approximately 2 nmole mg C^{-1} to >200 nmole mg C^{-1}) depending on the method used and experimental conditions employed during titrations (Sunda and Huntsman, 1991; Kogut and Voelker, 2001; Muller, Gulin, and Kalvoy, 2001; Laglera and van den Berg, 2003; Buck and Bruland, 2005; Hurst and Bruland, 2005). Moreover, the binding characteristics for L1 of Log K 12.9 and ligand concentrations of 33.5 nmole mg C^{-1} from the affinity analysis provide the most reasonable estimates of Cu^{2+} concentrations measured by the *in situ* flow-through system, and yet remained within the window of target values identified in the scientific literature. However, the site density of the weakest sites (L3 and L2) are higher than corresponding literature values (e.g., Apte, Gardner, and Ravenscroft, 1990; Buck and Bruland, 2005; Donat, Lao, and Bruland, 1994; Hering, Sunda, Ferguson, Morel, 1987; Sunda and Hanson, 1987; Zamzow, Coale, Johnson, and Sakamoto, 1998). These binding parameters were estimated from titration data collected with the Cu-ISE, whereas most of the studies in the scientific literature represent titration data collected with voltammetric methods. It is possible that voltammetric methods overestimate the concentration of Cu^{2+} by inclusion of some NOM-bound Cu in measurements of labile Cu, leading to underestimates of bound Cu (Hurst and Bruland, 2005). The difference in analytical techniques may explain some of the observed differences in parameter values.

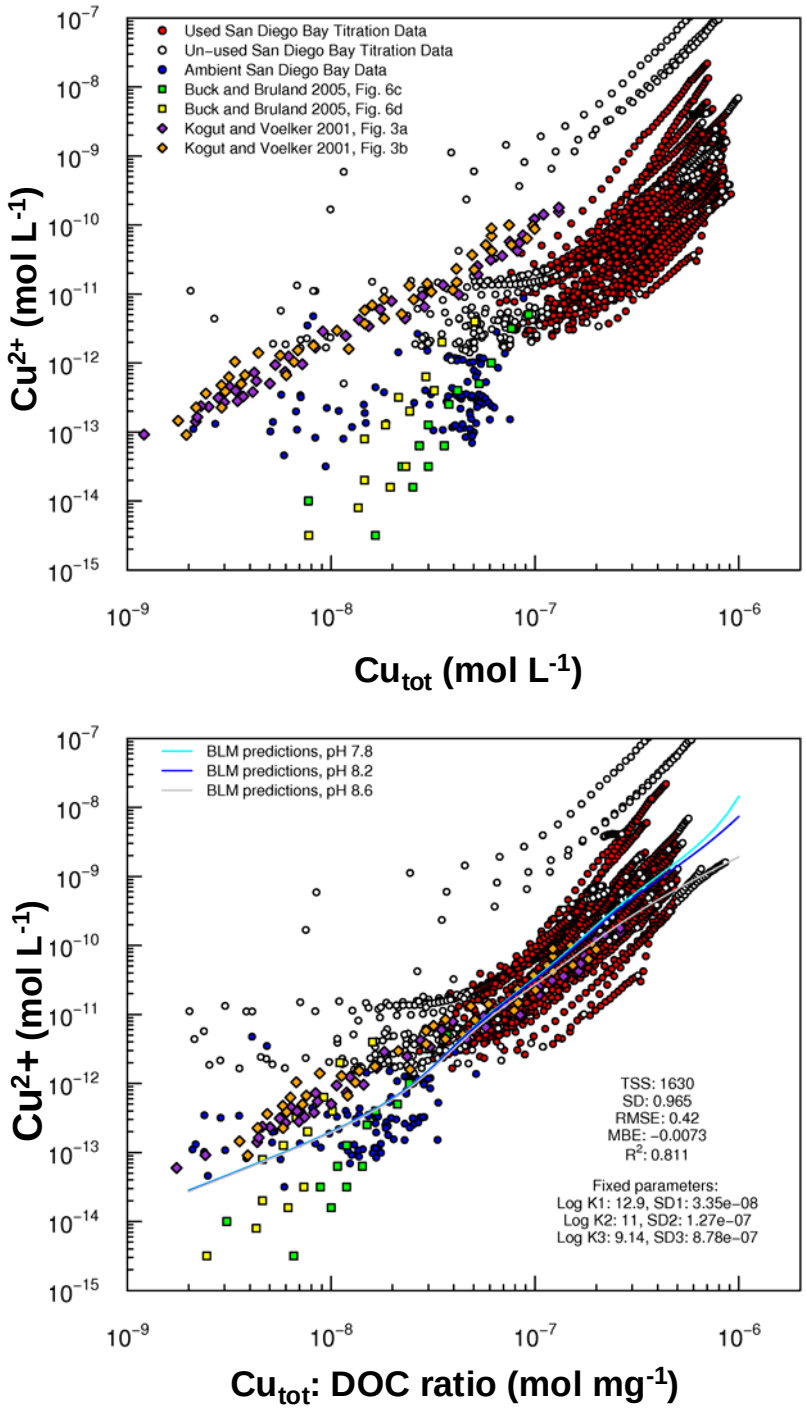


Figure 12. Measured and modeled copper speciation in San Diego Bay. Data from the calibration cruises, including excluded data are shown. For comparison, results from Kogut and Voelker (2001) and Buck and Bruland (2005) are included.

Model predictions for the contribution of each DOC ligand to bound Cu is shown in Figure 13. With the optimized parameter values, each individual ligand dominates in some region within the Cu_{tot} range of the ambient and titration data. The log Cu^{2+} concentrations that correspond to effects for the organisms tested range from -11 to -10, therefore, in this model, L2 generally plays the most important role in determining Cu toxicity for the studied organisms.

Inclusion of the hypothetical NOM binding site characteristics and H^+ interactions with NOM improved the performance of the seawater-BLM. However, inclusion of TSS as an additional source of copper binding ligands was required for the modeling to account for the effect of particulate organic carbon (POC) on copper speciation. The fraction of POC in TSS was not measured in CP-1156, which is unknown for San Diego Bay, and probably changes over time. Assuming that 20% of the TSS is particulate carbon is reasonably based on comparison at sites where POC and TSS have been measured. Furthermore, it is reasonable to expect that a particulate copper concentration would contribute to the distribution of metals in San Diego Bay, based on previous observations that approximately 20% of the copper in San Diego Bay is in a particulate form (Chadwick et al., 2004; Figure 14).

Predictions of Cu^{2+} from the resulting seawater-BLM model capture the general trend in the combined ambient and titration data for the calibration surveys (Figure 12). However, there is considerable variability within the measured Cu^{2+} data that are not related to DOC or differences in pH or TSS.

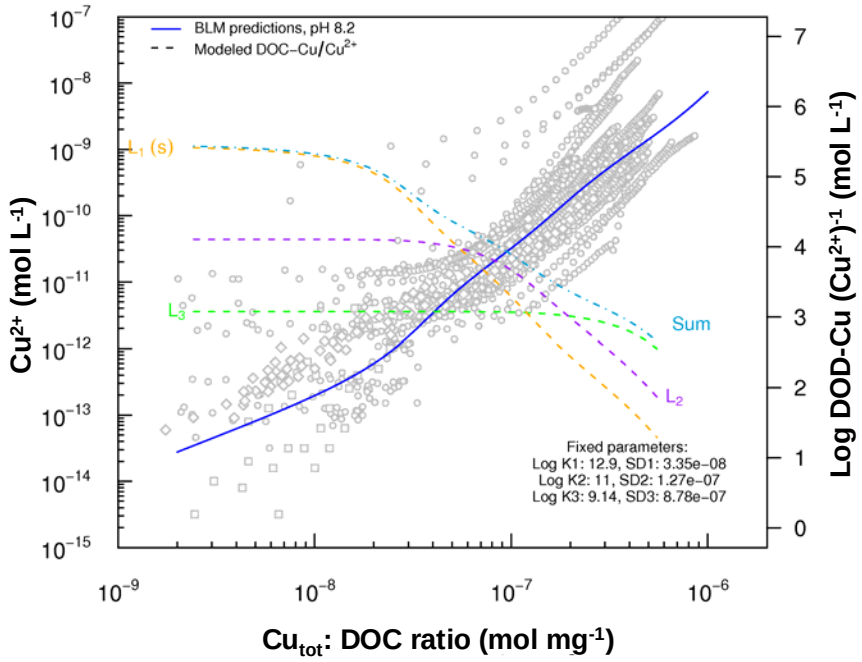


Figure 13. Measured and modeled copper speciation in San Diego Bay showing the relative importance of the three DOM ligands over a range of Cu concentrations. The points shown are the same as those in Figure 12.

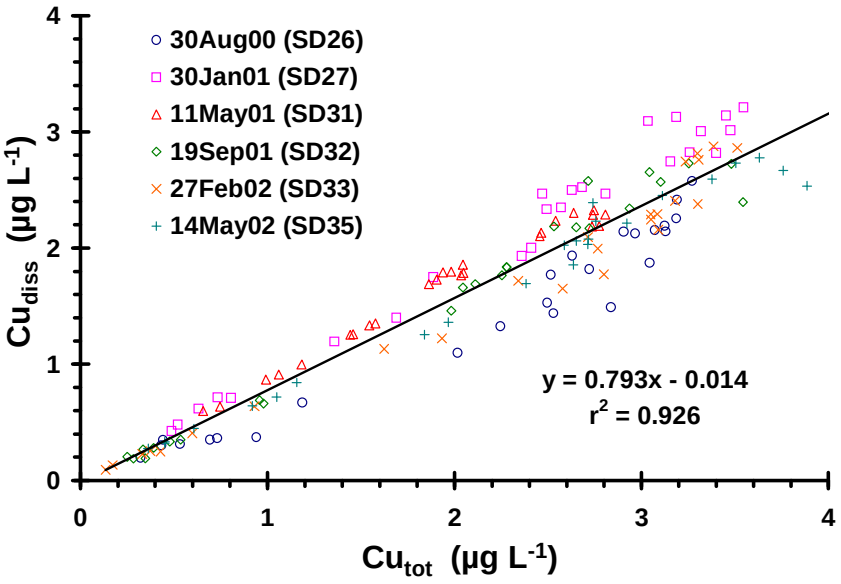


Figure 14. Relationship of Cu_{diss} to Cu_{tot} measured in ambient waters of San Diego Bay for SERDP Project CP-1156. In general, 79.3% of the copper is in the dissolved fraction.

4.3 4 B Validation of Seawater-BLM San Diego Bay

The sets of data from 11 May 2001 (SD31) and 19 September 2001 (SD32) were used to validate the models. The modeling factors determined from the calibration data were used and then applied to these two sets of data. The only inputs from the actual measurements are Cu_{tot}, DOC, TSS, and salinity. Prediction of the validation data resulted in a reasonable model fit (Figure 15 and Figure 16). Most predicted values (82%) were within a factor of five, but only 54% were within a factor of two of the reported values (Figure 16). It is not currently clear if the observed variability is due to differences in DOC quality or titration-specific systematic biases in measurement of Cu^{2+}.

4.3.5 C Calibration of Seawater-BLM for copper accumulation, San Diego Bay

Whole-body copper accumulation data for *M. galloprovincialis* and *S. purpuratus* (Rosen et al., 2008) were used to optimize parameters for Cu^{2+} and $CuOH^{+}$ binding to the biotic ligand. In this case, whole-body copper concentration was taken as a surrogate for copper bound to the hypothesized biotic ligand(s) that influences toxicity. This general approach of using a measurable surrogate for the biotic ligand has been used in previous applications of the BLM, i.e., by using Cu_{tot} bound to gills as a surrogate (e.g., Santore et al., 2001). Copper accumulation was adequately described using a two-site model (Figure 17). Copper EC50 values were greater than 4 µg L^{-1} for all the tests described in this report, suggesting that the low-affinity, high-capacity ligand is the only ligand required for prediction of toxicity. This finding is consistent with the spillover concept (Brown and Parsons, 1978, as cited in Ng and Wang, 2005; Wallace, Lee, and Luoma, 2003). Table 8 lists the optimized parameters for Cu^{2+} and $CuOH^{+}$ binding.

Table 8. Optimized parameters for copper binding to *M. galloprovincialis* and *S. purpuratus*.

Complex	Site density (nmol g-ww^{-1})	Maximum Cu binding (µg g-dw^{-1})	Log binding constant for Cu^{2+}	Log binding constant for $CuOH^{+}$
BL1	27.1	8.59	15.8	7.10
BL2	91100	28900	8.49	-0.209

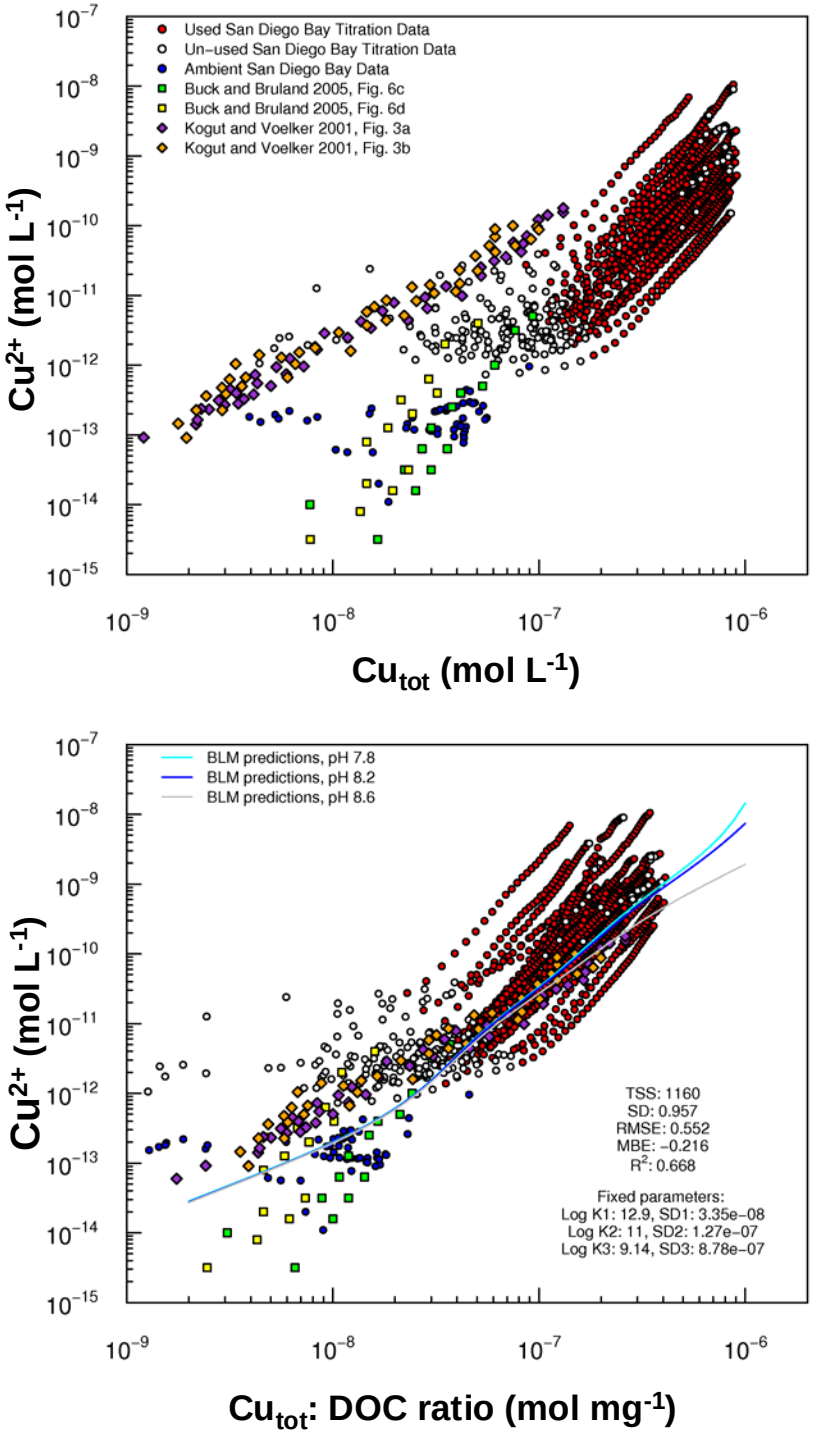
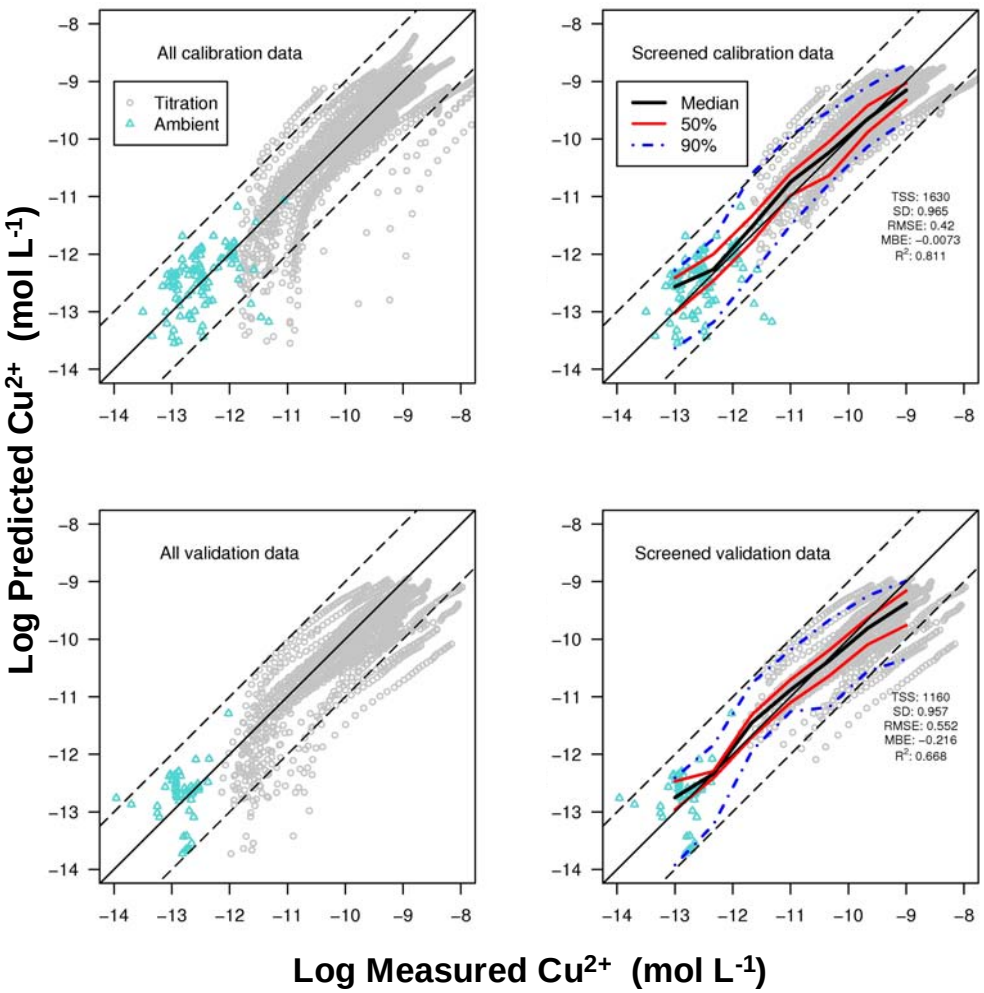


Figure 15. Application of the calibrated seawater-BLM Cu speciation model to the San Diego Bay validation data set. For comparison, results from Kogut and Voelker (2001) and Buck and Bruland (2005) are included.



Legend: TSS = total sum of squares, SD = standard deviation (population formula), RMSE = root mean square error, MBE = mean bias error.

Figure 16. A comparison of measured and seawater-BLM-modeled Cu^{2+} for San Diego Bay. Top plots show results for calibration data, while bottom plots show results for validation data. All statistics were calculated using log-transformed data. The straight solid line in each plot shows a 1:1 relationship, while the straight dashed lines are one order of magnitude above or below the 1:1 line. Other lines show the median or encompass 50% or 90% of the observations, as indicated.

4.3.6 D Calibration of Seawater-BLM for copper lethal accumulation

The complete seawater-BLM was used to predict copper accumulation for *M. galloprovincialis*, *Dendraster excentricus*, and *S. purpuratus* at the reported EC50s for San Diego Bay. Resulting modeled copper accumulation was used to estimate median lethal accumulation (LA50) values (Table 9). All biotic ligand-Cu species were included. For *Crassostrea gigas*, data from Pearl Harbor were used to estimate an LA50, since this organism was not studied in any of the San Diego trials. These LA50 estimates (Table 9) complete this calibration of the seawater-BLM. Accumulation experiments included estimates of LA50s by Rosen et al. (2008). For *M. galloprovincialis*, the LA50 was estimated as 49 µg g-dw^{-1} in the accumulation experiments, which is similar to the value used in the seawater-BLM (44 µg g-dw^{-1}). However, the LA50 for *S. purpuratus* was estimated as 142 µg g-dw^{-1} in the accumulation experiments, which is much lower than the value used in the BLM (438 µg g-dw^{-1}). Much lower EC50s in the accumulation experiments than those measured in the other toxicity tests (Figure 18) cause this discrepancy. The reason for the higher sensitivity of *S. purpuratus* in the accumulation experiments is currently unknown.

Table 9. Geometric mean LA50s used in the final seawater-BLM.

Organism	LA50 (nmol g-ww^{-1})	LA50 (µg g-dw^{-1})	Data source
M. galloprovincialis	137	43.7	San Diego
S. purpuratus	1380	438	San Diego
D. excentricus	394	117	San Diego
C. gigas	367	125	Pearl Harbor

The final seawater-BLM performed well for *D. excentricus* and *S. purpuratus*, but not as well for *M. galloprovincialis* (Figure 18). For *M. galloprovincialis*, all modeled values were within a factor of five, and 78% were within a factor of two of the reported values. For the other organisms, all modeled values were within a factor of two of the reported values, and a clear correlation exists between predicted and reported EC50s (Figure 18). The relatively poor performance for *M. galloprovincialis* appears to be due to the large amount of variability in the reported toxicity data that are not related to DOC concentration. Figure 18 shows the *M. galloprovincialis* data used in this calibration relative to a predictive model developed by Arnold (2005). In general, the *M. galloprovincialis* data show higher sensitivity to copper than previous results. Additionally, *M. galloprovincialis* EC50s from San Diego do not show a clear response to DOC, which is in contrast to other *Mytilus spp*. data (from San Francisco Bay and other estuaries in the U.S.) that did show a clear response with DOC and that did agree well with the predicted response in the BLM. It is not clear, therefore, why these data from San Diego Bay do not correlate as strongly as expected with DOC, but there does appear to be a component of the variability in these data that cannot be explained. Conversely, the *S. purpuratus* and *D. excentricus* EC50s from San Diego showed the expected increase in response to DOC concentration. The cause of the variability in *M. galloprovincialis* EC50s is currently unclear. Model residuals do not appear to be related to TSS, total zinc, salinity, or pH.

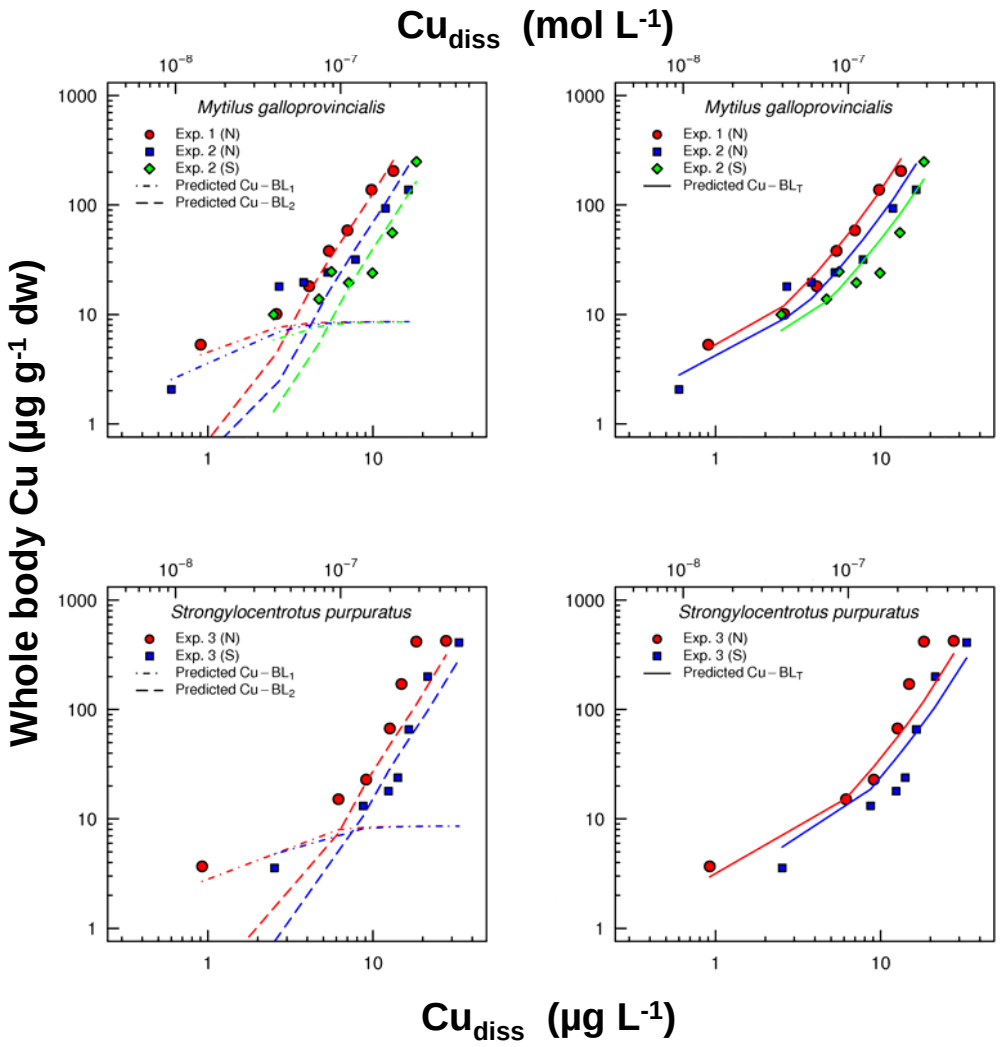


Figure 17. Measured and seawater-BLM-modeled whole-body copper accumulation for *M. galloprovincialis* and *S. purpuratus* in two waters from San Diego Bay. Table 8 lists parameters used for modeled values. Data are from Rosen et al. (2008). Cu_{diss} is given in µg L^{-1} in the bottom x-axis and in mol L^{-1} in the top x-axis. Both units are also provided in some of the figures below.

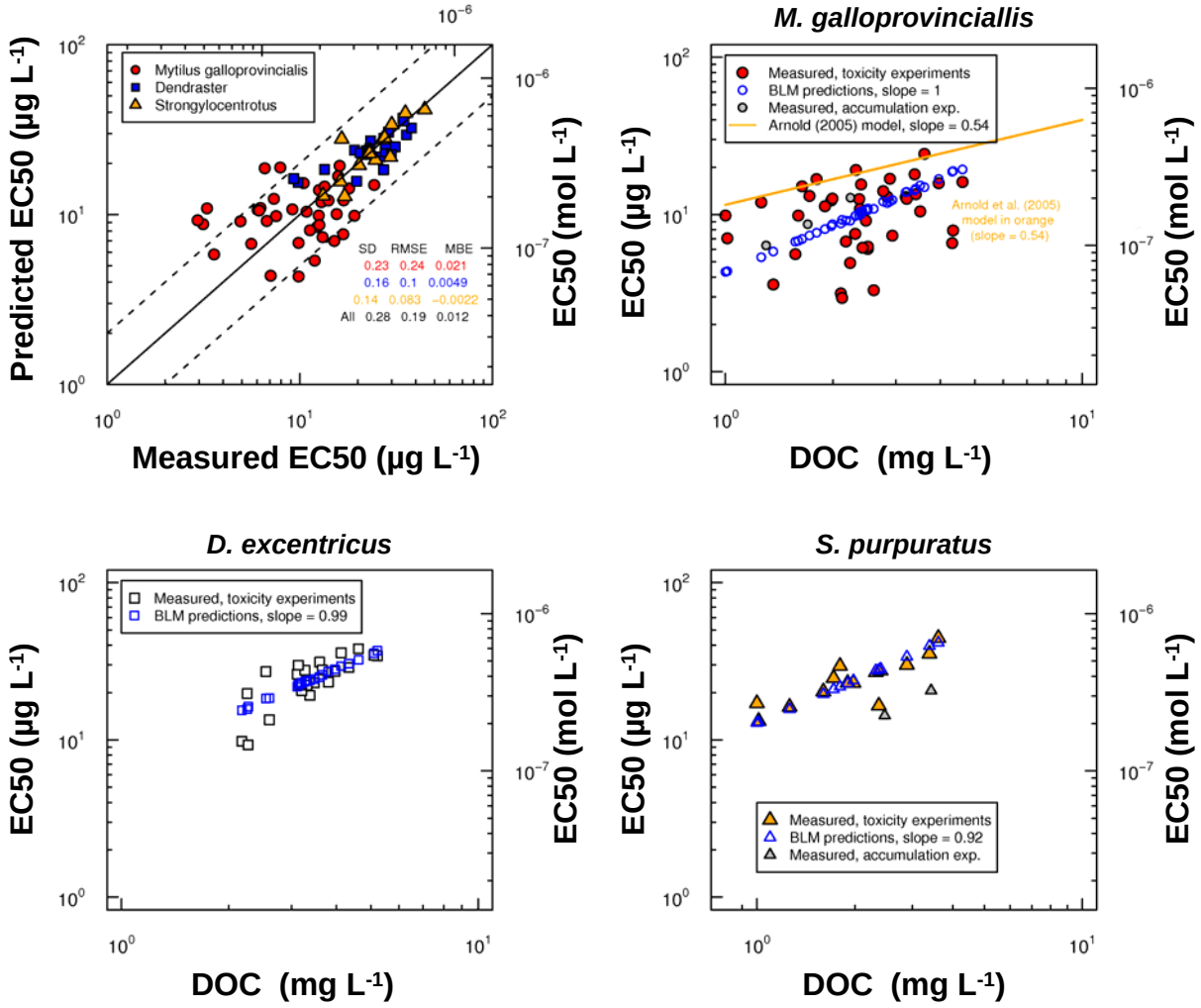


Figure 18. Measured and modeled Cu_{diss} EC50s for San Diego Bay.

4.3.7 Fate and Transport Model CH3D San Diego Bay

The CH3D model simulates advection processes caused by water currents and tides in San Diego Bay. The effect of tides is driven by tidal harmonic constants, which were obtained by calibration, and are prescribed at the open ocean boundaries (Figure 1, Wang et al., 1998). The sequence for the model simulation starts from quiescent initial conditions (zero water surface level for the entire bay), with tidal forcing at the model's ocean boundaries starting with the simulation ($t \geq 0$). The water surface elevation and tidal currents at every grid cell is simulated at a time step of 3 minutes, reaching simulated steady-state hydrodynamic conditions within 4 days. From the end of the 4th day, steady-state copper loading from various sources are introduced into the model from the various loading source locations. Simulation of F&T of copper, which is driven by the hydrodynamics simulation in CH3D, continues for another year so that copper concentration and its F&T patterns in the Bay reach steady state.

In general, water flows in San Diego Bay are driven by tides from the Pacific Ocean, which are assigned as the tidal forcing at the model's ocean boundaries. Tides in San Diego Bay are predominantly driven by diurnal (K1) and semi-diurnal (M2) components. Simulated water surface elevations range from ±70 cm during the neap tides to ±100 cm during the spring tides (Figure 19). In response to the principle of mass conservation, the ranges of water surface elevation also grow from the mouth toward the inner bay. Tidal flows enter into the bay through the mouth, where water is deep (~15–20 m), as the tidal flow propagates along the bay's axis, water depth decreases to ~10 m in Mid-Bay and <5 meters in South Bay. Following the conservation of mass, water mass accumulates inducing an increase in surface elevation on the shallower areas. In general, an average difference of ±5 cm exists for water surface elevation between mouth and inner bay locations, which is consistent with the results of a previous study (Wang et al., 1998).

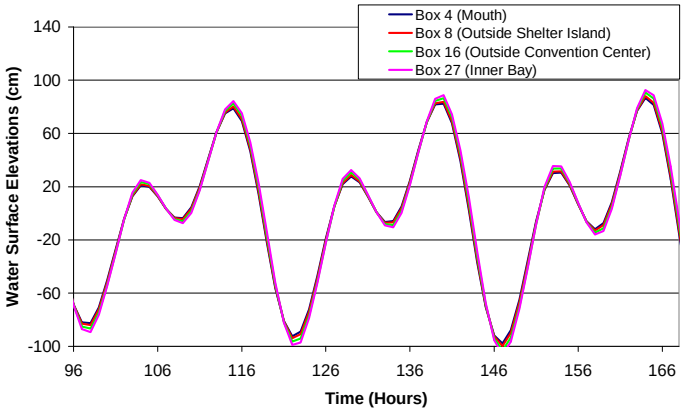


Figure 19. Predicted water surface elevations at several locations within San Diego Bay. The boxes are those designed in Figure 4.

A marked gradient exists in the magnitude of tidal currents within the Bay. Tidal currents are governed by multiple factors, including bathymetry, geometry of the Bay, bottom friction, etc. As a result, tidal current distributions differ from location to location; but current directions are restricted and follow the geometry of the Bay. The speeds of the tidal current range from ~15–50 cm s^{-1} near the mouth to over 65 cm s^{-1} in the channel bends and to less than 10 cm s^{-1} in the inner bay (Figure 20). In general, the simulated current direction follows the shape of the bay (Figure 21). Currents near the mouth are bi-directional, pointing north (~360°) and south (~180°) alternately, depending on the tidal stage. While simulated currents at box 4 and box 8 are going in or out of the bay, the direction of the flow follows the direction of the axis of the bay. While the direction in box 4 is north

(or south), the corresponding direction in box 8 is due east (or west). With the calibrated tidal harmonic constants assigned at the model's ocean boundaries, CH3D predicts both water surface elevations and tidal currents (both speed and direction) consistent with the results of Wang et al. (1998).

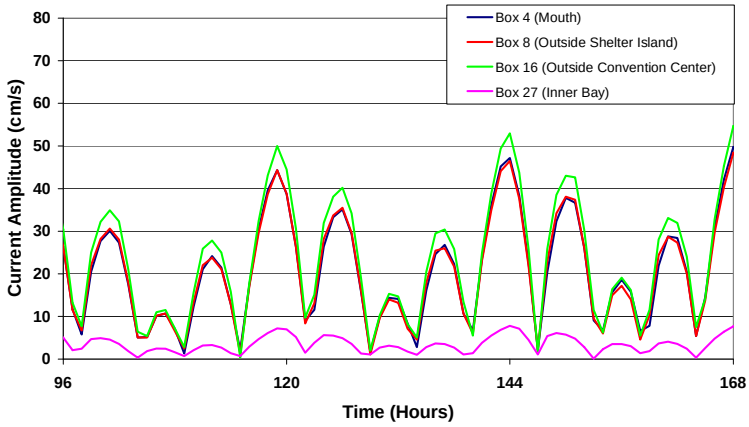


Figure 20. Predicted current amplitudes at four locations in San Diego Bay.

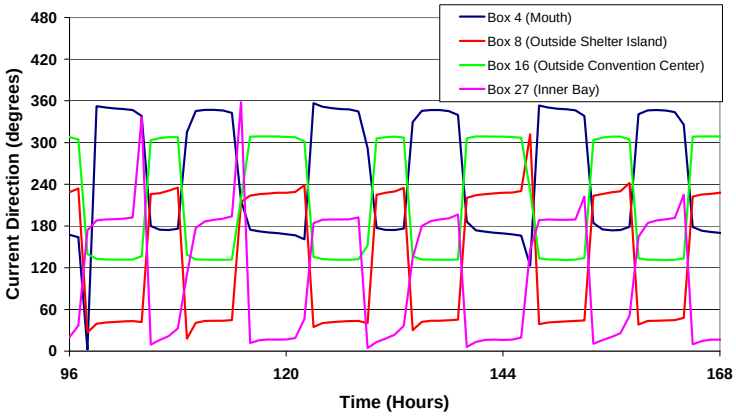


Figure 21. Predicted current direction at four locations in San Diego Bay. The angle is defined clockwise, with 0° and 360° indicating North and 90° East.

For the current study, CH3D was implemented to account for F&T of copper emanating from multiple sources. These sources are described in Section 3.3, and their distribution is shown in Figure 4. Sources include copper leached from ship hull paints of commercial and Navy vessels, watershed runoff, and ship-hull cleaning. For simulation of copper, data collected for the SERDP CP-1156 effort on 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35) were used for calibration and data collected on 11 May 2001 (SD31) and 19 September 2001 (SD32) for CH3D verification. For all the simulations, hydrodynamic forcing (tidal boundary and tidal harmonic constants) and Cu_{tot} loading remained the same. For each calibration simulation, a net settling velocity was assigned for Cu_{part}, which is lost from the water column to the sediment by way of gravitational settling. Since CH3D does not simulate gross settling or resuspension processes, a net settling, which can be conceptually interpreted as the net effect of copper loss from total settling subtracted from total resuspension, was assigned and used as a calibration parameter so that simulated Cu_{tot} concentrations reach optimal approximation to the field data. Further evaluation of the predicted capacity of the model indicated the important role that the bathymetry plays in resuspension, with the shallower parts of the bay (boxes 25 to 27) having a

different net settling effect. Local conditions (i.e., bathymetry, winds) affect resuspension in this area and result in a different settling rate, which was modeled as a continuous linear decrease in settling rate, as explained below.

For model validation in San Diego Bay, the distributions of the above parameters were predicted using the net settling velocity that was assigned for each of the four calibration simulations. Therefore, four sets of predicted concentration distributions were modeled for each of the two validation data sets. The integrated model predicts F&T of the contaminants, including water-column and sediment-bound portions.

4.3.8 Fate and Transport Model CH3D Pearl Harbor

The CH3D model simulates water currents and tides in Pearl Harbor. Historical tide gauge data measured near the entrance of the harbor were used and fine-tuned as the boundary conditions (Figure 1). The model simulation starts from quiescent initial conditions (zero water surface level for the entire Harbor). Tidal forcing at the model's ocean boundaries is turned on at the start of the simulation ($t \geq 0$), with CH3D simulating water surface elevations and tidal currents at every grid cell at a time-step of 2 minutes. Simulated steady-state hydrodynamic conditions in Pearl Harbor are reached within 2 days. From the end of the second day, steady-state copper loadings from various sources are included in the model. The simulation of F&T of copper continues for another 6 months so that copper concentrations and its F&T patterns reach steady state.

In general, flows in Pearl Harbor are driven by ocean tides from the Pacific Ocean, which are assigned as the tidal forcing at the model's ocean boundaries. Tides in Pearl Harbor are predominantly driven by diurnal (K1) and semi-diurnal (M2) components. Simulated water surface elevations range from ±50 cm during spring tides to ±25 cm during neap tides (Figure 22), with negligible differences of water surface elevation in the different lochs for amplitude and phase. Tidal flows enter Pearl Harbor from the south entrance, from which the deep navigation channel extends into the harbor. Tidal flows propagate along the channel into the West Loch, East Loch and Middle Loch. Distance from the entrance to the northern shore of the east loch is about 8 km, taking less than 12 min of travel time for the K1 and M2 tides. The open configuration of the harbor domain reduces the phase lag of the tidal flows in the various lochs to a minimum.

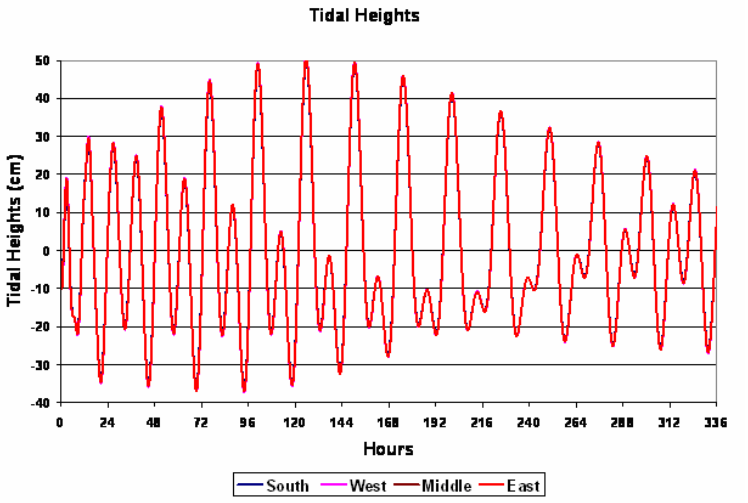


Figure 22. Predicted water surface elevations at four locations in Pearl Harbor: South Branch, West Loch, Middle Loch, and East Loch.

As is the case in San Diego Bay, tidal currents in Pearl Harbor are governed by multiple factors, including bathymetry, geometry of the harbor and bottom friction. As a result, tidal current distributions are different from location to location in the harbor, with current directions restricted and following the geometry (shape) of the harbor. The magnitude of the tidal currents range from ~15–20 cm s^{-1} near the south part of the channel to less than 5 cm s^{-1} in the lochs (Figure 23). The magnitude of the simulated currents in the lochs is comparable to the less than 5 cm s^{-1} measured at the East Loch[6], and the 2 cm s^{-1} measured between North and East Loch (Koehl, 2007).

CH3D is implemented in Pearl Harbor to account for F&T of copper emanating from multiple sources. These sources include copper leached from ship hull paints from commercial and Navy vessels, watershed runoff, and ship-hull cleaning, as described in Section 3.3. Earley et al. (2007) collected the data used in the demonstration in four sampling events: 15–18 March 2005 (Event 1), 18–20 October 2005 (Event 2), 23–27 January 2006 (Event 3), and 15–19 May 2006 (Event 4). Events 1, 2, and 4 are for the dry season, and Event 3 is for wet season. Samples from surface water (~ 1-m deep) from the Harbor were collected at eight locations (Figure 5). The parameters measured included TSS, DOC, TOC, Cu_{diss}, and Cu_{tot}. Data from Events 1 and 4 were used for calibrating CH3D, then the model parameters from these calibrations were applied for model validation with data from Event 2. For the validation, the calibrated model parameters were upheld, and only the field data of TSS, DOC, and pH for Event 2 were used.

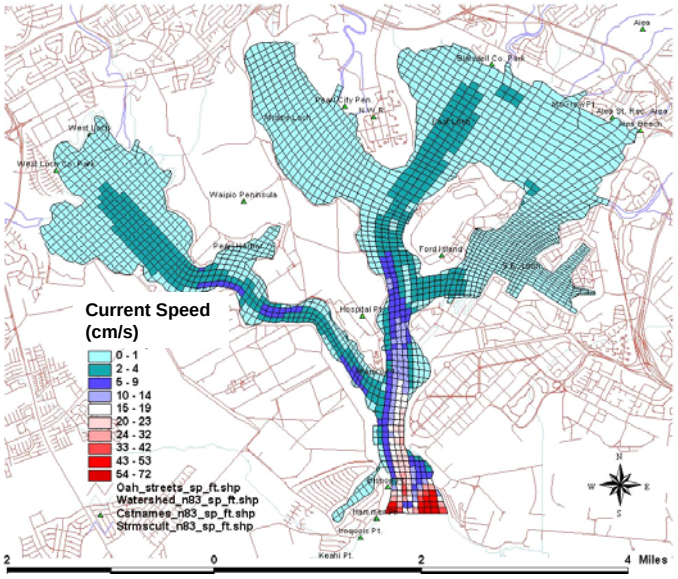


Figure 23. Predicted tidal current amplitudes in Pearl Harbor.

4.3.9 Integrated Model: CH3D/Seawater-BLM

In the integrated CH3D/seawater-BLM model, the BLM is an enhancement to the CH3D model and is embedded in CH3D. At every time-step, CH3D simulates hydrodynamics, including water surface elevations and currents, and transport of contaminants. The BLM is accessed as a dynamic link library (DLL) to operate after the transport routine in CH3D is executed. This approach allows for continuing modeling with CH3D in time-steps, with the option to execute the BLM modeling at any desired time step. When running the integrated CH3D/seawater-BLM model for San Diego Bay,

[6] Personal communication with Brad Davidson, SSC Pacific.

in order to allow for the transport of copper to reach steady-state conditions, the simulation of the hydrodynamic and F&T model, CH3D, is performed continuously for 419 days (1 year + 54 days). Then the seawater-BLM algorithm in the integrated model is called at every hour after day 405 for the next 14 days. In the case of Pearl Harbor, the integrated model simulates the hydrodynamic and F&T for 194 days (6 month + 14 days), the first 180 days are to ensure that the F&T of copper reaches steady state, then the BLM algorithm is called every hour after day 180 for 14 days. Inputs for seawater-BLM include Cu_{tot}, salinity, DOC, TSS, and pH. Cu_{tot} concentrations are predicted by CH3D while the other input parameters (salinity, DOC, TSS, and pH) are from field measurements. Output of seawater-BLM includes Cu_{part}, Cu_{diss}, and Cu^{2+}. The output parameters predicted by the CH3D/seawater-BLM model are stored at every grid cell hourly for 14 days.

Output. Field data are divided into two groups, one for model calibration and the other for model validation. For San Diego Bay, calibration data include the datasets for 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35). Data for validation include those from 11 May 2001 (SD31) and 19 September 2001 (SD32). For Pearl Harbor, the data for calibration are from15–18 March 2005 (Event 1) and 15–19 May 2006 (Event 4), and from 23–27 January 2006 (Event 3), the data from 18–20 October 2005 (Event 2) were used for validation, but only with parameters from events 1 and 4, as 23–27 January 2006 (Event 3) was considered different because it is the only one for the wet season.

For all the simulations, hydrodynamics forcing and Cu_{tot} loading remained the same. For each calibration simulation, a net settling velocity was assigned for Cu_{part}, which is lost from the water column to the sediment bed by way of gravitational settling. Since CH3D does not simulate gross settling or resuspension processes, a net settling, which can be conceptually interpreted as the net effect of copper loss from total settling subtracted from total resuspension, is assigned and used as a calibration parameter so that simulated Cu_{tot} concentrations reach optimal comparison with the field data. Therefore, settling velocity is the only parameter that it is adjusted in the calibration for optimization of the matching between predicted and measured Cu_{tot} concentrations throughout each harbor. In San Diego Bay, the initial approach was to use a constant homogeneous settling velocity for the whole Bay, resulting in under prediction of the concentrations of Cu_{tot} and Cu_{diss} in the shallower areas in South Bay (boxes 25 to 27 in Figure 4). These results can be explained as the effect of wind-driven resuspension in this area of the bay, affecting the net settling velocity. This problem was corrected by assuming a linear decrease in settling velocity going from box 25 in the bay throughout box 26 to a minimum value in box 27. Table 10 shows the settling velocities used for boxes 2 to 24 for the four calibration scenarios and the value used for box 27.

Settling patterns in Pearl Harbor were previously studied qualitatively (Earth Tech, 2007). Figure 24 shows that settling is greatest in Middle Loch, followed by West Loch and East Loch. Using these qualitative patterns, the model was calibrated by adjusting the net settling velocity in different lochs until the best fit between model-predicted and measured copper concentrations was attained. The calibrated settling velocities in the different regions within the harbor are shown in Table 11.

Table 10. Constant settling velocities used for boxes 2 to 24 for the four calibration scenarios in San Diego Bay. A linear decrease was assumed from box 25 through box 26 to the minimum value given for box 27.

	30 August 2000 (SD26)	30 January 2001 (SD27)	27 February 2002 (SD33)	14 May 2002 (SD35)
Settling velocity Boxes 2 to 24 (cm hr^{-1})	4.3	19.5	5.0	5.5
Settling velocity Box 27 (cm hr^{-1})	2.1	5.0	2.4	2.7

Table 11. Calibrated settling velocities for model simulations in Pearl Harbor.[7]

	Settling Velocity (cm hr^{-1})				
	Event 1	(Event 3)	Event 4	Event 2(a) Validation	Event 2(b) Validation
Middle Loch	14	7.5	12	14	12
West Loch	4	4	2	4	2
East Loch	1	1	1	1	1
Southeast Loch	30	27	35	30	35
Central Channel	10	7.5	7.5	10	7.5

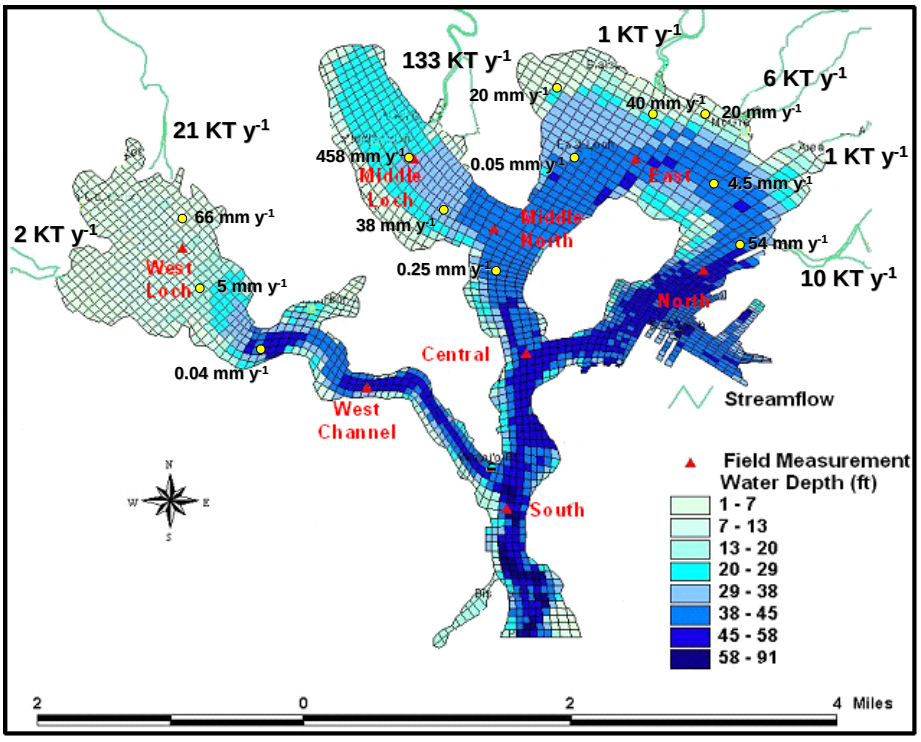


Figure 24. Empirically estimated settling patterns in Pearl Harbor. Sediment input (KT yr^{-1}) and settling rates (mm yr^{-1}) for solids concentrations under no hydrodynamic disturbance condition.

[7] Events 2(a) and 2(b) are for model verification using the calibrated parameters for Events 1 and 4, respectively.

4.3.10 A Calibration of Integrated CH3D/Seawater-BLM Model San Diego Bay

Results from integrated CH3D/seawater-BLM model calibration simulations include concentration distributions of Cu_{tot}, Cu_{diss}, Cu_{part}, and Cu^{2+}. For San Diego Bay, model outputs are stored hourly for 14 days at each model grid cell, each of which has multiple model layers in the water column. To compare with the field data, copper concentrations are simulated for 24 locations along the axis of the bay (from the bay mouth to South Bay). These locations correspond to boxes 2 to 27 sampled under SERDP Project CP-1156, excluding boxes 6 and 9, which correspond to bayside harbors heavily used for civil marinas, and box 1, which is considered representative of coastal waters outside San Diego Bay (Figure 4). The concentration data set at each of the 24 locations for each model run has 336 data points (hourly data for 14 days). The volume averaged daily mean (mean value predicted each day or the average of 14 data points) at each location was used for analysis and comparison with the concentrations measured for SERDP Project CP-1156 at each of the boxes. The mean daily maximum and daily minimum represent the range in the predicted values. Following the performance criteria, the concentrations of Cu_{tot}, Cu_{diss}, and Cu^{2+} are analyzed and discussed. These measured concentrations are from seawater samples integrated during transit through each box, and were collected at different stages in the daily tidal excursion. To account for tidal excursion, all of the measured data were corrected for tidal advection to an average tidal condition, which is done by displacing each sample location by the corresponding tidal excursion at that location and then interpolating back onto the original box grid.

30 August 2000 (SD26). Correspondence for Cu_{tot} is good between the integrated CH3D/seawater-BLM model results and the measured data. The comparisons between modeled results and field data for Cu_{tot} concentrations are shown in Figure 25 and Figure 26. At each box location, the average daily mean of the 14 days of the steady-stage model simulation are compared with the field data. The simulated daily mean Cu_{tot} concentrations behave in similar fashion as the field data, increasing from low values (0.2–0.7 µg L^{-1}) near the mouth to 2-3 µg L^{-1} in Mid-Bay and peaking around the Naval Station (boxes 20 and 21). In general, measured Cu_{tot} are within the ranges enveloped by the daily maximum and daily minimum, except in boxes 24 and 25 located by the inner region of the bay. The similitude between the two sets of data is also evidenced by their correlation (Figure 26) with the mean Cu_{tot} simulated for each box explaining 93% of the variance of the measured data, a slope close to one (i.e., 0.98) and a minimum intercept (0.17 µg L^{-1}). Tidal effects on the copper transport are revealed in the ranges enveloped by daily maximum and daily minimum. Tidal effects are large near the mouth regions and reach a maximum around box 7 (outside Shelter Island), where current is strong. Tidal effects fluctuate and decrease gradually toward the southern Bay. An advantage of the CH3D/seawater-BLM model is the capacity to predict copper distributions with great spatial detail, as shown for the Cu_{tot} predicted for 30 August 2000 (SD26) (Figure 27).

There was a tendency to over-predict Cu_{diss} with the integrated CH3D/seawater-BLM model on the data for 30 August 2000 (SD26) (Figure 28 and Figure 29). Cu_{diss} concentrations follow the same general pattern in concentration as Cu_{tot}, and are more than 70% of the Cu_{tot} for this scenario. The integrated model predicted values that follow the same pattern of concentrations in the bay, but with average values that are larger than the measured values. This over-prediction resulted in a lower correlation that only explains 89% of the variance of the measured data, and a relatively larger intercept (0.37 µg L^{-1}) (Figure 29) than for the Cu_{tot} (0.17 µg L^{-1}) (Figure 26).

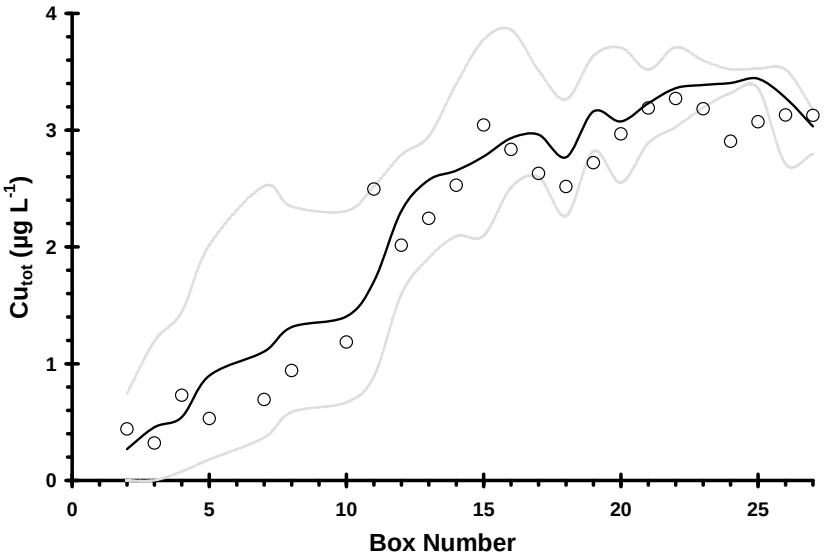


Figure 25. Distribution of predicted and measured Cu_{tot} (µg L^{-1}) in San Diego Bay on 30 August 2000 (SD26). Field data (○) from SERDP CP-1156 and predicted mean concentration (dark line) and range (space between grey lines) from integrated CH3D/seawater-BLM model. The same symbol and lines are used in the corresponding figures below.

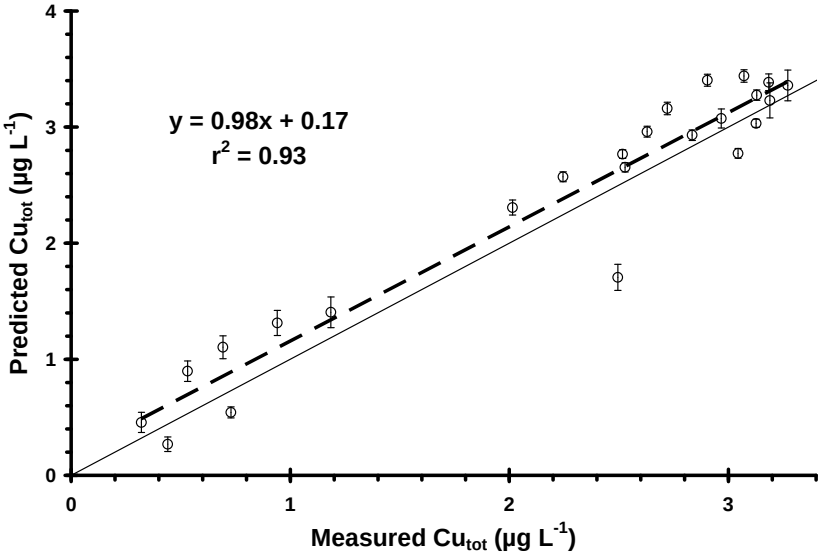


Figure 26. Predicted versus measured Cu_{tot} (µg L^{-1}) for 30 August 2000 (SD26). Measured Cu_{tot} from SERDP CP-1156 and predicted daily mean (○, with ±1 sd) by the integrated CH3D/seawater-BLM model, with regression (broken line). The solid line is the one-to-one ratio. The same symbol and lines are used in the corresponding figures below.

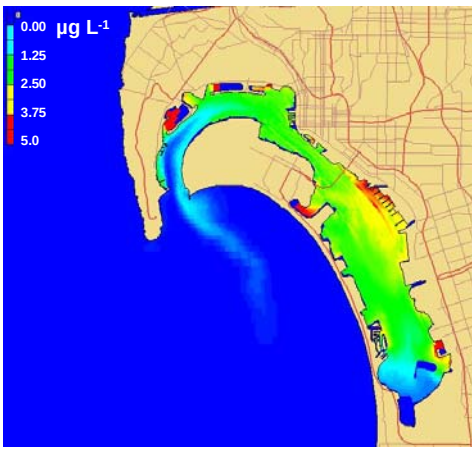


Figure 27. Cu_{tot} (µg L^{-1}) contour distribution predicted by the integrated CH3D/seawater-BLM model for 30 August 2000 (SD26) in San Diego Bay.

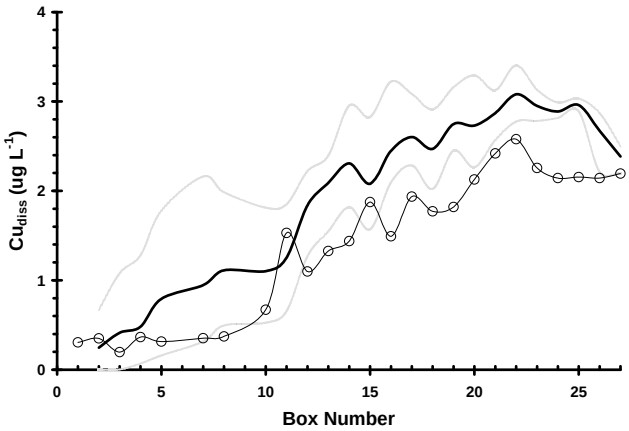


Figure 28. Cu_{diss} (µg L^{-1}) in San Diego Bay for 30 August 2000 (SD26).

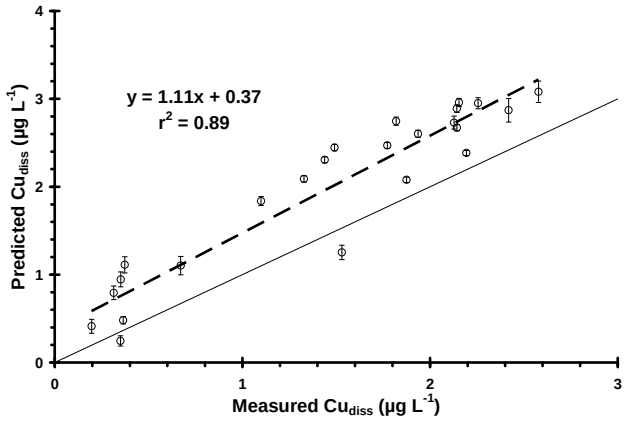


Figure 29. Predicted versus measured Cu_{diss} (µg L^{-1}) for 30 August 2000 (SD26).

Since the predicted concentrations for Cu_{diss} tended to be higher than measured values, it is no surprise that predicted Cu^{2+} also tended to be higher than measured. Predicted free copper concentrations also tended to over-emphasize the gradients in Cu^{2+} (pCu) throughout the bay in comparison to the measured values. For the sampling event of 30 August 2000 (SD26), as well as for the rest of the sampling events, the Cu-ISE in the flow-through system measured pCu values that were fairly uniform (mean 13.0 ±0.10 for 30 August 2000, SD26) (Figure 30), with a slight decrease towards the inner bay. Predicted pCu values have a more pronounced spatial pattern, with lower mean values at the mouth of the bay, increasing above measured values and remaining fairly constant throughout most of the bay, with a slight decrease in the back of the Bay. However, mean predicted values are always within one order of magnitude of the measured ones, with an average difference of 0.33 ±0.37 pCu units. Note that similarly to the pH scale, the pCu scale is in orders of magnitude (inverse logarithm of the concentration). The combination of almost constant measured Cu^{2+} and the differences in the values are reflected in the comparison (not shown) with 0% of the variance explained. This is an artifact of correlation analysis, making it not applicable for constant values, which negates the approach, proposed for performance criteria of having the predicted values explaining ≥60% of the variance of the measured values.

Minimum and maximum predicted values are extremely different from measured Cu^{2+} at the mouth of the bay. Predicted minimum and maximum Cu^{2+} in boxes 2 and 3 are up to four orders of magnitude different to the measured values (Figure 30). In comparison, as indicated above, mean predicted values in the rest of the bay are within an order of magnitude of the measured values. There are several possible explanations for this, including the effect of miniscule changes in Cu_{tot} or Cu_{diss}, or differences in the characteristics of DOM in coastal waters in comparison to Bay waters.

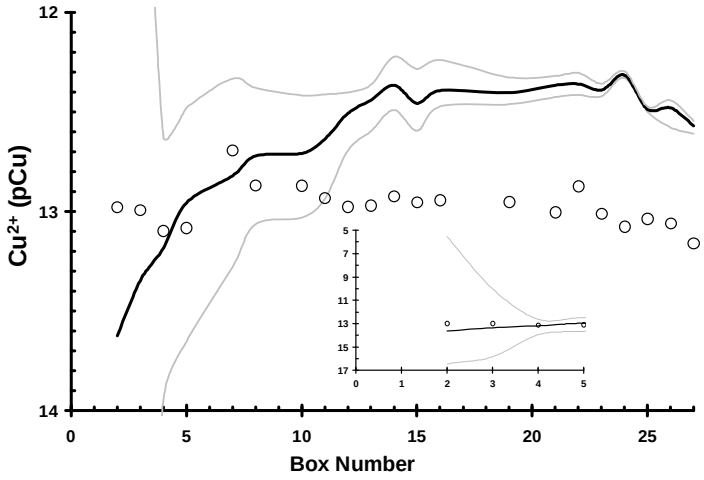


Figure 30. Cu^{2+} (expressed as pCu) in San Diego Bay for 30 August 2000 (SD26). The insert shows the pCu range predicted for boxes 1 to 5.

30 January 2001 (SD27). For this scenario, simulated daily mean Cu_{tot} behaved in similar fashion as the field data, increasing from 0.2–0.7 µg L^{-1} near the mouth to 2–3 µg L^{-1} in the mid-Bay and peaking at 3 to 4 µg L^{-1} around the Naval Station (boxes 21 and 22) (Figure 31). In general, measured Cu_{tot} is enveloped by the daily maximum and daily minimum, except in the inner Bay (boxes 23–27), where measured Cu_{tot} decrease from 3.5 µg L^{-1} at box 23 to about 2.5 µg L^{-1} at box 27, while predicted Cu_{tot} decrease from 3.5 µg L^{-1} to about 0.8 µg L^{-1}. Although the trend of decrease toward the inner bay is the same between model and measurements, there is a discrepancy in the magnitude of the decrease. Comparison between measurements and predictions indicate a correspondence

within the expected performance criteria, with 90% of the variance explained by the predicted values (Figure 32), a slope close to one (0.99) and a small intercept (0.04 µg L^{-1}) (Figure 32).

Tidal effects on the copper transport are revealed in the ranges enveloped by daily maximum and daily minimum. Tidal effect is large near the mouth regions and reaches a maximum around box 7 (outside Shelter Island), gradually decreasing towards the South Bay.

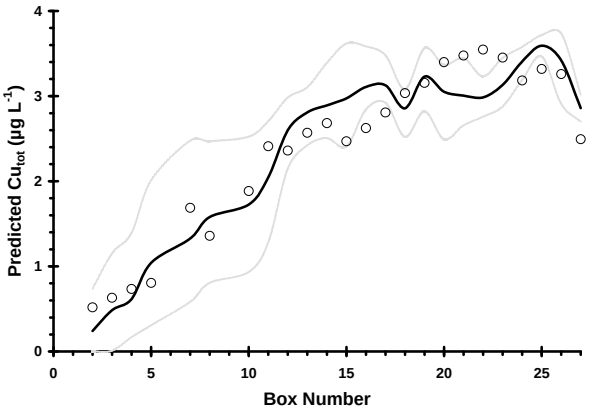


Figure 31. Cu_{tot} (µg L^{-1}) in San Diego Bay for 30 January 2001 (SD27).

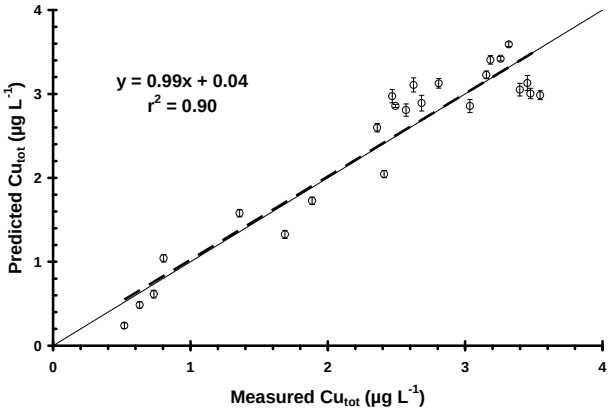


Figure 32. Predicted versus measured Cu_{tot} (µg L^{-1}) for 30 January 2001 (SD27).

Simulated Cu_{diss} also represent the measured values quite well. Their comparisons are shown in Figure 33, and Figure 34 for 30 January 2001 (SD27). For this scenario, Cu_{diss} constitute more than 70% and behave similarly to Cu_{tot}. The agreement between these values includes the sharp drop in concentration measured for the inner bay (boxes 25 to 27). The efficiency of the model to predict the measured values is substantiated by the correlation with 89% of the variance in the measured values explained by the predicted ones, a slope close to one (0.98) and a small intercept (0.03 µg L^{-1}) (Figure 34). An example of the resolution of the concentrations predicted by the integrated model is given in Figure 35.

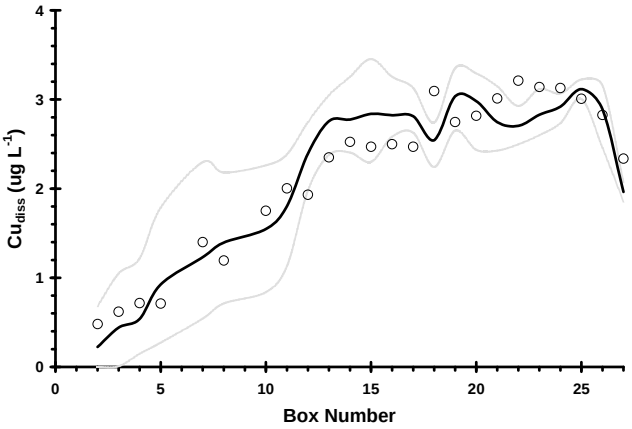


Figure 33. Cu_{diss} (µg L^{-1}) in San Diego Bay for 30 January 2001 (SD27).

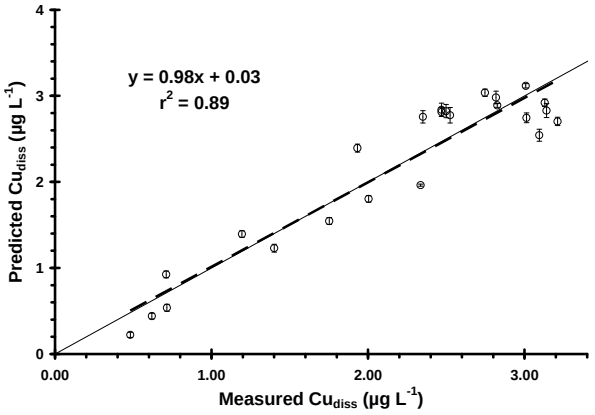


Figure 34. Predicted versus measured Cu_{diss} (µg L^{-1}) for 30 January 2001 (SD27).

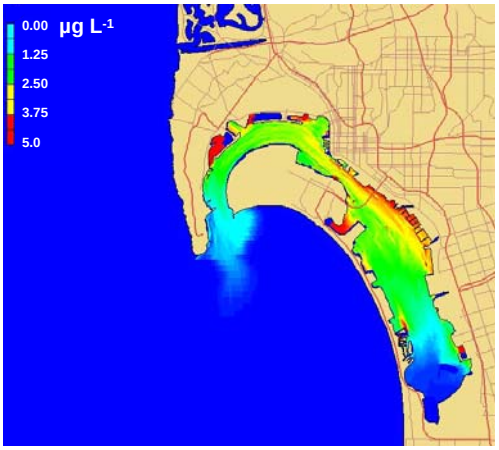


Figure 35. Predicted Cu_{diss} (µg L^{-1}) distribution contours for 30 January 2001 (SD27).

Predicted Cu^{2+} are up to five orders of magnitude smaller or four orders of magnitude larger than the measured ones in the coastal area of the bay. Figure 36 show the Cu^{2+} for the bay on 30 January 2001 (SD27). Measured Cu^{2+} fluctuate around 11–12 near the mouth and increase nearly to a constant of 12 for most of the bay, decreasing slightly toward the inner bay. Simulated Cu^{2+} indicate concentrations up to five orders of magnitude lower in the mouth of the bay, to values in the same order of magnitude from boxes 4 to 26.

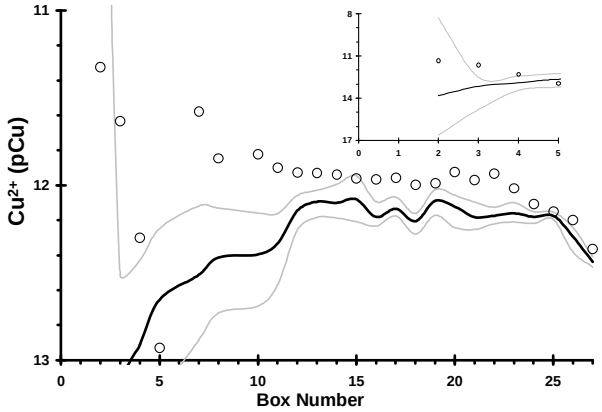


Figure 36. Cu^{2+} (pCu) in San Diego Bay for 30 January 2001 (SD27).

27 February 2002 (SD33). There is a difference in this scenario between the measured and predicted trends for the area highly influenced by coastal waters in the bay. While measured Cu_{tot} remained relatively constant at low concentrations from boxes 1 to 7, and then had a steep increase to box 13, predicted values had a constant increase from low values to those measured in box 13, with the rest of the boxes having very similar measured and predicted values (Figure 37). Nonetheless, the two trends are very similar as supported by their correlation with 93% of the variance of the measured data being explained by the predicted data (Figure 38). However, the tendency to over-predict the lower concentrations at the mouth of the bay skews the correlation to a larger intercept (0.68 µg L^{-1}).

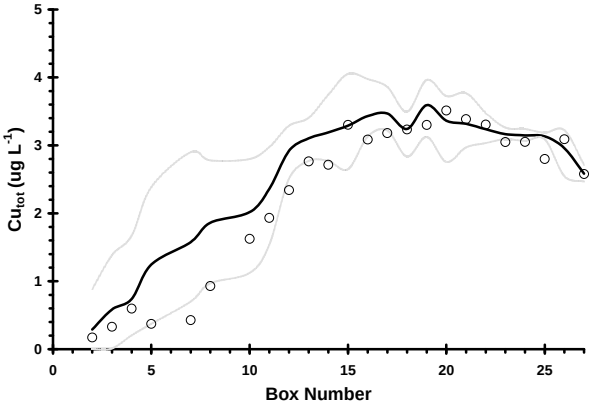


Figure 37. Cu_{tot} (µg L^{-1}) in San Diego Bay for 27 February 2002 (SD33).

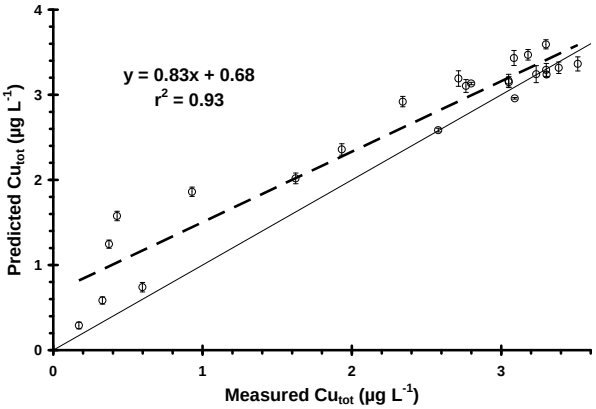


Figure 38. Predicted versus measured Cu_{tot} (µg L^{-1}) for 27 February 2002 (SD33).

Cu_{diss} behave similarly to those of Cu_{tot} for 27 February 2002 (SD33). Predicted values seem to represent better concentrations measured in the area of the bay influenced by coastal waters. However, in the back of the bay there is a tendency to under-predict the measured concentrations (Figure 39). The predictions are within the performance criteria, with predicted values explaining 89% of the variance of measured ones, an intercept of 0.45 µg L^{-1}, probably due to the influence of the over-prediction in the mouth of the bay (Figure 40). Cu_{diss} are more than 70% of Cu_{tot} for this scenario.

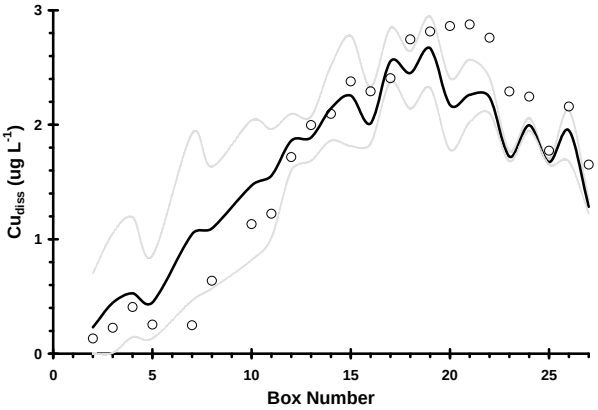


Figure 39. Cu_{diss} (µg L^{-1}) in San Diego Bay for 27 February 2002 (SD33).

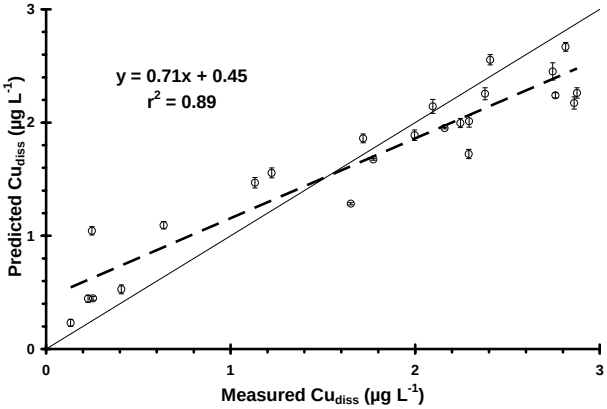


Figure 40. Predicted versus measured Cu_{diss} (µg L^{-1}) for 27 February 2002 (SD33).

Cu^{2+} concentrations were relatively constant throughout the bay on 27 February 2002 (SD33). Figure 41 and Figure 42 show the Cu^{2+} concentration distributions. Measured Cu^{2+} fluctuate around 13 to 14 near the mouth and increase nearly to a constant of 12.5 for most of the bay, slightly decreasing toward the inner bay. Simulated Cu^{2+} values behave in a very similar fashion and the good match between them persist throughout the regions, especially the decrease of Cu^{2+} concentrations towards the inner bay that is captured in model results and measurements. Predicted values are within an order of magnitude of the measured ones, but for the mouth of the bay.

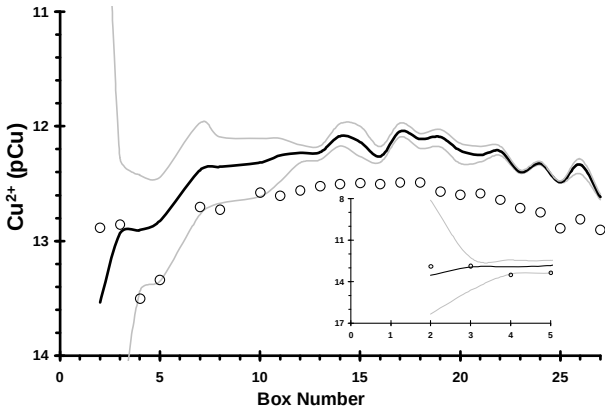


Figure 41. Cu^{2+} (pCu) in San Diego Bay for 27 February 2002 (SD33).

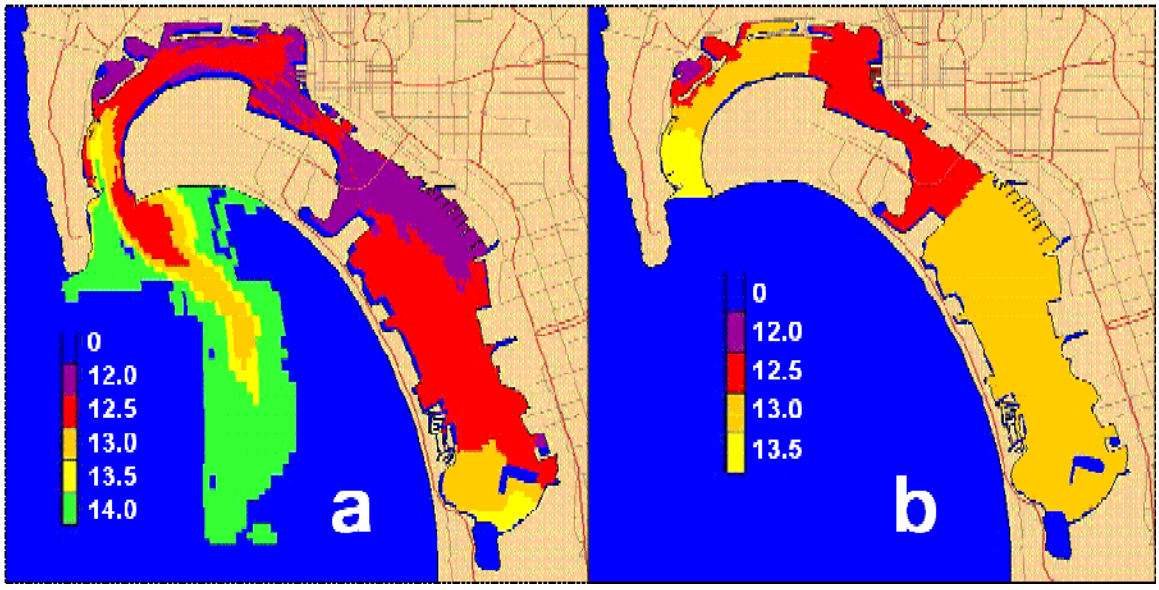


Figure 42. Cu^{2+} (pCu) contours for 27 February 2002 (SD33) predicted with (a) the integrated CH3D/ seawater-BLM model, and (b) field data.

14 May 2002 (SD35). The similitude between measured and predicted values is also within the performance criteria for this scenario. Simulated daily means and field data for Cu_{tot} behave in similar fashion, increasing from low values (0.2–0.7 µg L^{-1}) near the mouth to 2-3 µg L^{-1} in the mid to inner bay (Figure 43 and Figure 44). Measured Cu_{tot} is low at the mouth of the bay, increases from Naval Station (~3 µg L^{-1}) (Boxes 21 and 22) towards the inner bay (~4 µg L^{-1} in box 26), with only the concentration at box 27 dropping down to ~ 2.8 µg L^{-1} (Figure 43). This pattern in the increase of

Cu_{tot} towards the inner bay is different from the copper distributions from all the other scenarios. In general, measured Cu_{tot} are within the ranges enveloped by the daily maximum and daily minimum, except in box 27 in the innermost regions of the bay. Simulated Cu_{tot} exhibit a pattern consistent with those for the other scenarios and explains 90% of the variance of the measured values for this scenario (Figure 44).

The pattern in the distribution of measured Cu_{diss} in 14 May 2002 (SD35) is not as extreme as the measured Cu_{tot}. Figure 45 and Figure 46 show the Cu_{diss} for this scenario. Cu_{diss} are more than 55% of Cu_{tot} for this scenario. Predicted Cu_{diss} seem to mimic measured values well throughout the regions, except in the inner regions, model results are slightly over-estimated compared with the measurements. The similitude of these distributions is supported by their correlation with 89% of the variance of the measured data explained by the predicted values (Figure 46).

Measured Cu^{2+} (expressed as pCu) is very constant throughout the bay. Figure 47 and Figure 48 show the pCu distributions. Measured pCu has an average of 12.50 ±0.08 pCu units for the whole bay (Figure 47). Simulated Cu^{2+} show more variation in the values and are within an order of magnitude of the measured values for most of the bay, but the mouth (box 2 only), where predicted values are between one and two orders of magnitude lower (Figure 47). A comparison between the distributions of predicted and measured Cu^{2+} is given in Figure 48.

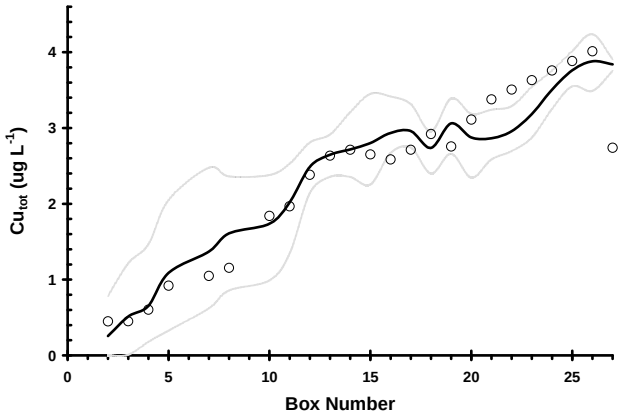


Figure 43. Cu_{tot} (µg L^{-1}) in San Diego Bay for 14 May 2002 (SD35).

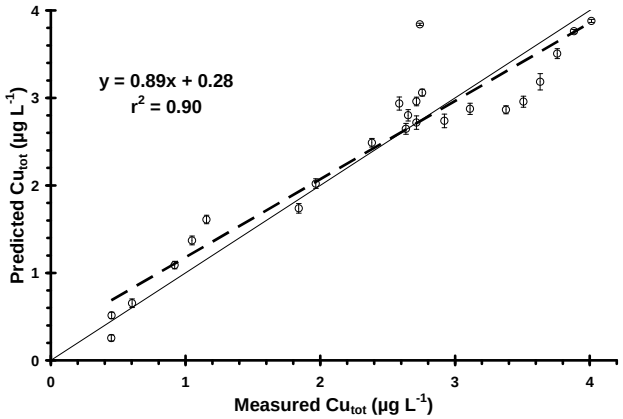


Figure 44. Predicted versus measured Cu_{tot} (µg L^{-1}) for 14 May 2002 (SD35).

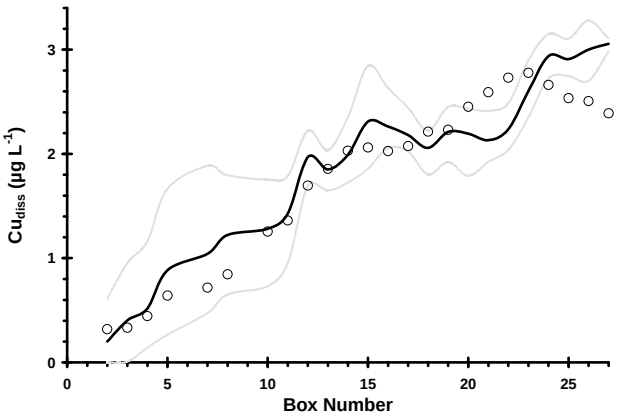


Figure 45. Cu_{diss} (µg L^{-1}) in San Diego Bay for 14 May 2002 (SD35).

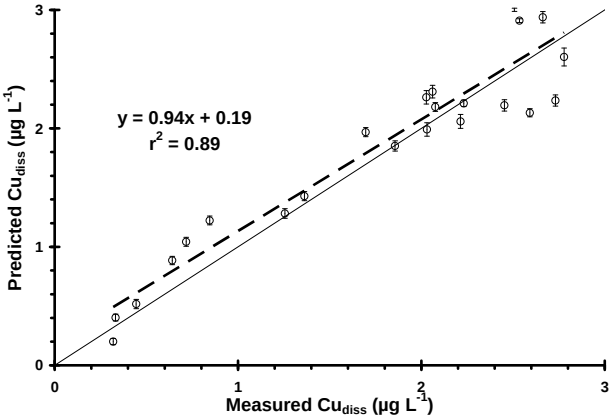


Figure 46. Predicted versus measured Cu_{diss} (µg L^{-1}) for 14 May 2002 (SD35).

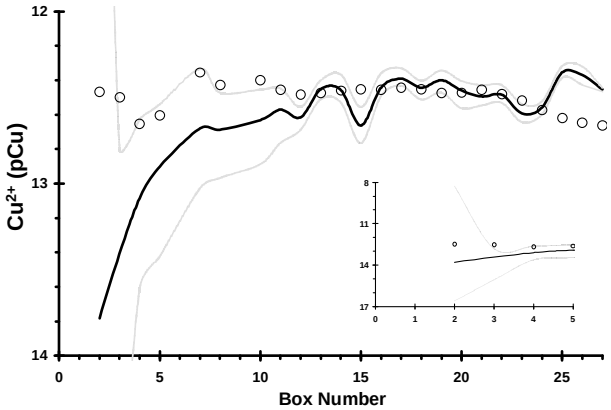


Figure 47. Cu^{2+} (pCu) in San Diego Bay for 14 May 2002 (SD35).

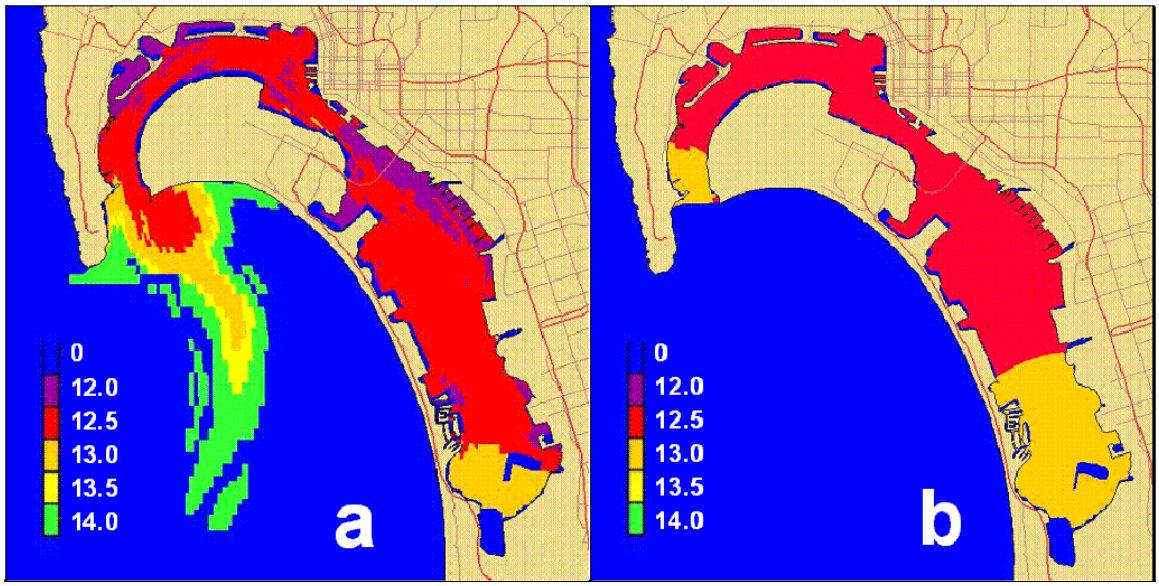


Figure 48. Cu^{2+} (pCu) contours for 14 May 2002 (SD35). Predicted by (a) the integrated CH3D/ seawater-BLM model and (b) field data.

The comparisons between predicted and measured Cu_{tot} and Cu_{diss} concentrations are within the performance criteria. The statistic values for these comparisons in San Diego Bay are shown in Table 12. These statistics indicate that for Cu_{tot} and Cu_{diss}, the integrated model explains that better than 89% of the variance of the measured values, which is better than the 60% required by the performance criteria (Table 4).

Table 12. Statistics from the calibration of the integrated model in San Diego Bay. Values are derived from the comparisons between predicted and measured concentrations.

Sampling date	Cu_{tot}			Cu_{diss}		
	% Variance	Intercept	Slope	% Variance	Intercept	Slope
30 August 2000 (SD26)	93	0.17	0.98	89	0.37	1.11
30 January 2001 (SD27)	90	0.04	0.99	89	0.03	0.98
27 February 2002 (SD33)	93	0.68	0.83	89	0.45	0.71
14 May 2002 (SD35)	90	0.28	0.89	89	0.19	0.94

4.3.11 B Calibration of Integrated CH3D/Seawater-BLM Model Pearl Harbor

For Pearl Harbor, to compare with the field data, simulated copper concentrations at eight locations distributed throughout the harbor are used (Figure 5). Concentration data set at each of the stations has 336 data points (hourly data each day or 24 concentrations for 14 days). For each location during each event, daily mean values (mean value of the 24 concentrations) are used for comparison and analysis. Following the performance criteria, the concentrations of Cu_{tot}, Cu_{diss}, and Cu^{2+} are analyzed and discussed.

15–18 March 2005 (Event 1). Figure 49 shows comparisons between model results and field data of Cu_{tot} at the eight stations (Figure 5). These stations are North, Central, South, East Loch, Middle

North, Middle Loch, West Loch, and West Loch Channel. Predicted Cu_{tot} behave in a fashion similar to that of the field data, increasing from the South channel (near the mouth) low values (0.2–0.3 µg L^{-1}) to 0.5–0.6 µg L^{-1} in the Central channel, reaching a maximum in the North location (Southeast Loch), gradually decreasing to 0.5–0.8 µg L^{-1} in East Loch, Middle Loch, and West Loch. Tidal effects on copper transport are revealed in the descending trends from the South to Central, North, and West Loch. Tidal effects in the East Loch and Middle Loch are reduced to a minimum. Overall, predicted values explain 77% of the variance of the measured Cu_{tot} (Figure 49). Figure 50 shows the contours of Cu_{tot} predicted by the integrated model for 15–18 March 2005 (Event 1) in Pearl Harbor. Overall, copper concentrations are low (below 1 µg L^{-1}) for most of the regions, except in regions near the freshwater stream discharges and the Naval Submarine Base, where predicted Cu_{tot} attain values as high as 3 µg L^{-1}. Figure 51 shows the comparison between predicted and measured Cu_{diss} for 15–18 March 2005 (Event 1). This plot indicates that the model explains 77% of the variance of the measured values when predictions are regressed against observations. Cu_{diss} behave in a fashion similar to those of Cu_{tot}, and Cu_{diss} are more than 80% of the Cu_{tot} for this event. Figure 52 shows the predicted Cu^{2+} (pCu) values for 15–18 March 2005 (Event 1). Predicted pCu are between 13 and 14 for almost all the regions, except at the South location where predicted pCu increases to 14. There are no *in situ* Cu^{2+} measurements in Pearl Harbor for comparison with model results.

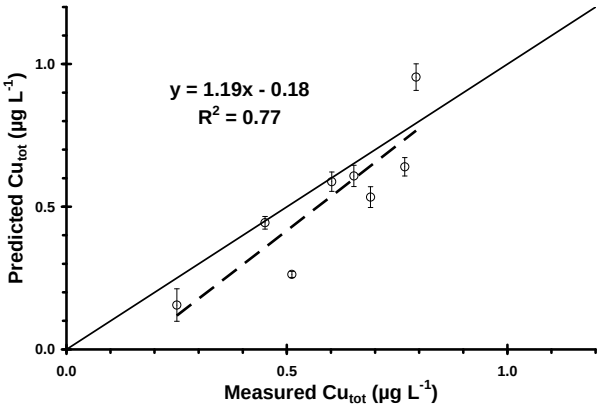


Figure 49. Predicted versus measured Cu_{tot} for 15-18 March 2005 (Event 1) in Pearl Harbor.

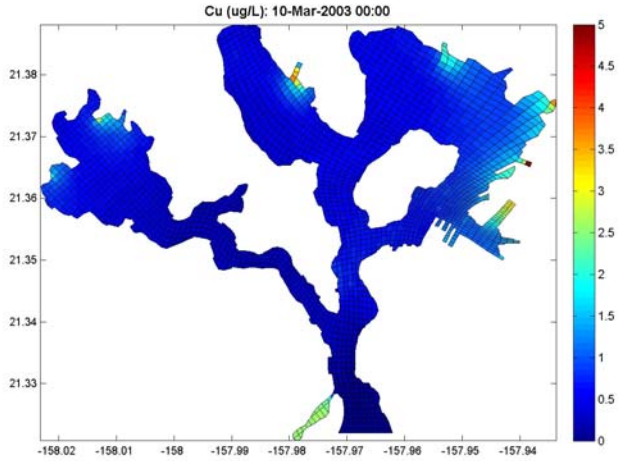


Figure 50. Contours of predicted Cu_{tot} from the integrated CH3D/seawater-BLM model for 15–18 March 2005 (Event 1) in Pearl Harbor.

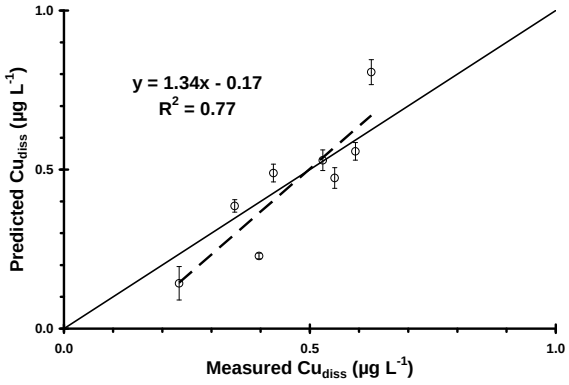


Figure 51. Predicted versus measured Cu_{diss} for 15–18 March 2005 (Event 1) in Pearl Harbor.

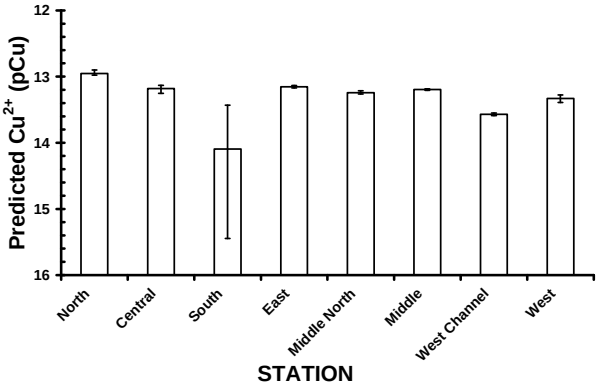


Figure 52. Predicted Cu^{2+} (expressed as pCu) in Pearl Harbor for 15–18 March 2005 (Event 1).

15–19 May 2006 (Event 4). Comparison between predicted and measured concentration of Cu_{tot} for this event are shown in Figure 53. As the figure indicates, the predicted daily mean distribution of Cu_{tot} is very similar to the measured data. With concentrations increasing from the South channel station (near the mouth) with low predicted (0.2 µg L^{-1}) and measured (0.5 µg L^{-1}) values, to 0.6–0.7 µg L^{-1} in the Central channel, reaching a maximum in the North location (Southeast Loch), gradually decreasing to 0.5–0.8 µg L^{-1} in the East Loch, Middle Loch, and West Loch. Tidal effects on copper transport are revealed in the descending trends from the South to Central, North, and West Loch. Tidal effects in the East Loch and Middle Loch are reduced to a minimum. Overall, the predicted Cu_{tot} can explain 61% of the variance of the measured concentrations (Figure 53) for this event. The geographical concentration distribution of Cu_{tot} predicted by the integrated model is shown in Figure 54. This predicted gradient is similar to the one for 15–18 March 2005 (Event 1), with overall Cu_{tot} below 1 µg L^{-1} for most of the regions, except in regions near the freshwater stream discharges and the Naval Submarine Base, where predicted Cu_{tot} attain values as high as 3 µg L^{-1}. Figure 55 shows the comparison between predicted and measured Cu_{diss} for 15–19 May 2006 (Event 4), and indicates that the predicted values cannot predict the variance in the measured data (9%) because of the minimal variance in the Cu_{diss} measured in this event (range, 0.49–0.58 µg L^{-1}). Though the predicted range (0.130.68 µg L^{-1}) is also minimal, the measured Cu_{diss} essentially is a constant value. Cu_{diss} represents more than 70% of the Cu_{tot} for this event. The integrated model predicts Cu^{2+} concentrations (pCu) that are between 13 and 14 for almost all the regions (Figure 56), except at the South location where the predicted concentration decreases to 14. As mentioned above, no *in situ* measured Cu^{2+} data are available from Pearl Harbor for comparison with model results.

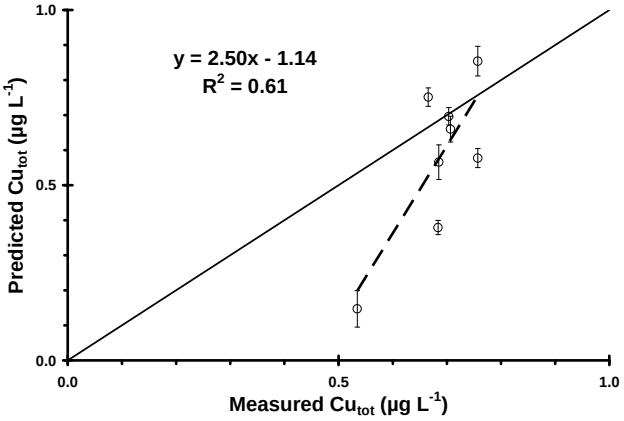


Figure 53. Predicted versus measured Cu_{tot} in Pearl Harbor for 15–19 May 2006 (Event 4).

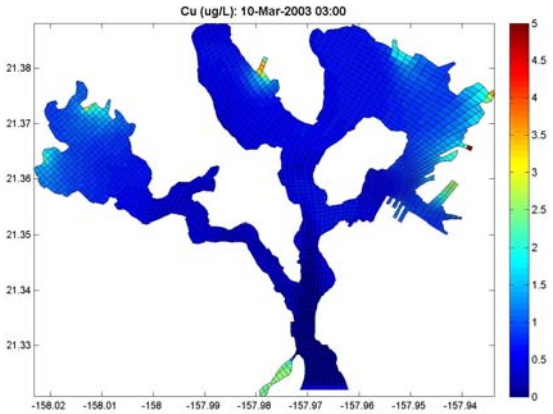


Figure 54. Cu_{tot} distribution predicted by the integrated model for 15–19 May 2006 (Event 4) in Pearl Harbor.

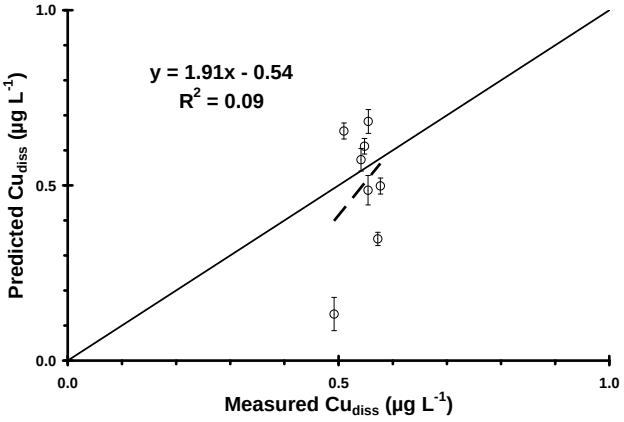


Figure 55. Predicted versus measured Cu_{diss} for 15–19 May 2006 (Event 4) in Pearl Harbor.

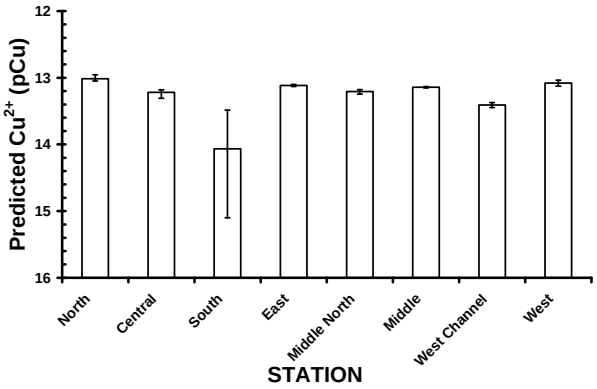


Figure 56. Predicted Cu^{2+} (expressed as pCu) in Pearl Harbor for 15–19 May 2006 (Event 4).

23–27 January 2006 (Event 3). Unlike the events of 15–18 March 2005 (Event 1), 18–20 October 2005 (Event 2), and 15–19 May 2006 (Event 4), data for 23–27 January 2006 (Event 3) were collected during a wet season. Since storm runoff load constitutes 16% of the Cu_{tot} load in Pearl Harbor, copper loads from storm runoff were distributed over a 4-month period from November to February.

Comparisons between predicted and measured Cu_{tot} at the eight stations for this event are shown in Figure 57, and the predicted Cu_{tot} gradients are shown in Figure 58. These comparisons show that the predicted daily means of Cu_{tot} behave in similar fashion as the field data. With concentrations in the South channel station (near the mouth) at values ~1 µg L^{-1} to between 1 and 1.3 µg L^{-1} in the Central channel, reaching a maximum of 1.7 µg L^{-1} in station North (Southeast Loch), gradually decreasing to between 1.1 to 1.4 µg L^{-1} in East Loch, Middle Loch, and West Loch. Tidal effects on copper transport are revealed in the descending trends from the South to Central, North, and West Lochs, and minimal tidal effects in the East and Middle Lochs. Cu_{tot} predicted by the integrated model explain 94% of the variance of the measured concentrations in surface waters. Overall, while Cu_{tot} for this event are higher than those for the other three events, they are still low, with concentrations below 2 µg L^{-1} for most of the regions, except in regions near the freshwater stream discharges and the Naval Submarine Base, where predicted Cu_{tot} attain values as high as 4–5 µg L^{-1}.

Figure 59 shows the model-measurement comparisons of Cu_{diss} for 23–27 January 2006 (Event 3). This plot indicates that the predicted values explain 72% of the variance of the measured concentrations. Cu_{diss} behave in a fashion similar to those of Cu_{tot}, and Cu_{diss} are more than 70% of Cu_{tot} for this event. Figure 60 shows the predicted Cu^{2+} values (pCu). Predicted pCu are just below 13 for almost all the regions except at the South location where predicted pCu reaches 13. No measured Cu^{2+} data are available for comparison with model results.

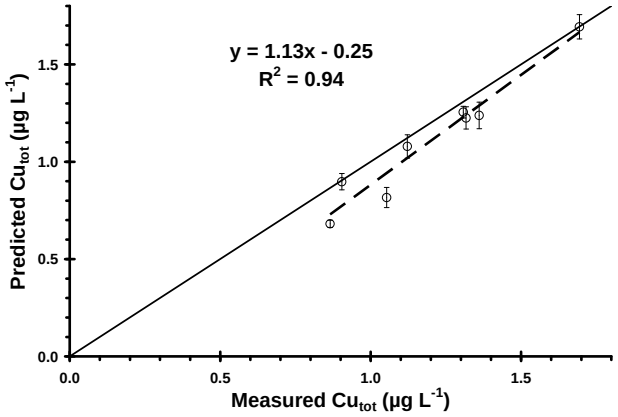


Figure 57. Predicted versus measured Cu_{tot} in Pearl Harbor for 23–27 January 2006 (Event 3).

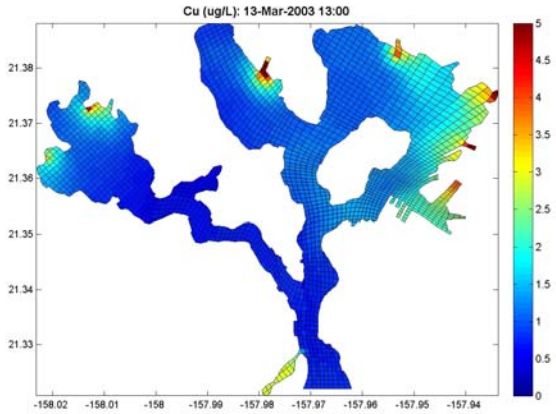


Figure 58. Predicted Cu_{tot} gradients in Pearl Harbor for 23–27 January 2006 (Event 3).

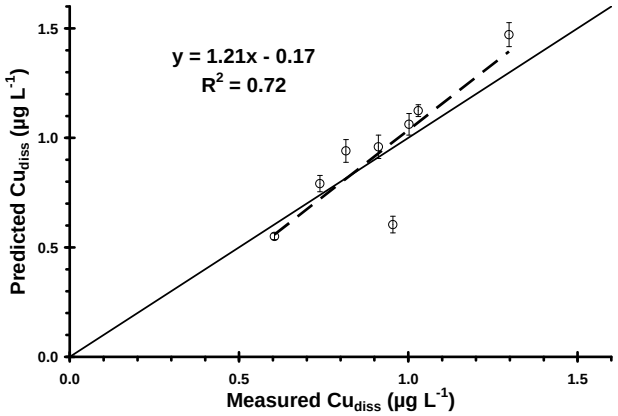


Figure 59. Predicted versus measured Cu_{diss} for 23–27 January 2006 (Event 3).

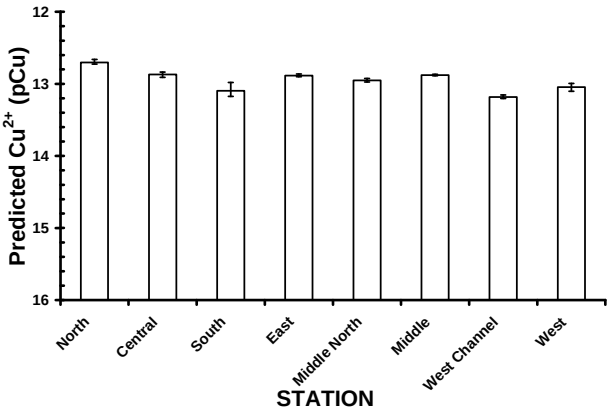


Figure 60. Predicted Cu^{2+} (expressed as pCu) in Pearl Harbor for 23–27 January 2006 (Event 3).

The effect by the range in concentration and/or the lack of a gradient over the prediction capability of the integrated model is evident in these calibrations. For Cu_{tot} the model performs better for 15–18 March 2005 (Event 1) (Cu_{tot} range, 0.25–0.79 µg L^{-1}; ΔC 0.54 µgL^{-1}) and 23–27 January 2006 (Event 3) (Cu_{tot} range, 0.87–1.69 µg L^{-1}; ΔC 0.83 µgL^{-1}) than for 15–19 May 2006 (Event 4) (Cu_{tot} range, 0.53–0.76 µg L^{-1}, ΔC 0.22 µgL^{-1}), when the range in concentration is minimal (Table 13). The results for Cu_{diss} are even more drastic in this respect, and the model is within performance criteria for the cases where the range in Cu_{diss} concentration is from 0.23–0.62 µg L^{-1} , ΔC 0.54 µgL^{-1} (15–18 March 2005–Event 1) and from 0.60–1.30 µg L^{-1} , ΔC 0.69 µgL^{-1} (23–27 January 2006–Event 3). In contrast, the model cannot predict concentrations in the case where the range in concentration is minimal, 0.49–0.58 µg L^{-1}; ΔC 0.09 µgL^{-1} (15–19 May 2006–Event 4; Table 13). The integrated model evaluation procedure requires a significant gradient in concentration.

Table 13. Statistics from the calibration of the integrated model in Pearl Harbor.

Sampling date	Cu_{tot}			Cu_{diss}		
	% Variance	Intercept	Slope	% Variance	Intercept	Slope
15–18 March 2005 (Event 1)	77	-0.18	1.19	77	-0.17	1.34
15–19 May 2006 (Event 4)	61	-1.14	2.50	9	-0.54	1.91
23–27 January 2006 (Event 3)	94	-0.25	1.13	72	-0.17	1.21

4.3.12 C Validation of Integrated CH3D/Seawater-BLM Model San Diego Bay

Validation of the integrated model in San Diego Bay was performed by applying the main characteristics used in its calibration for the scenarios from 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35) to predict the scenarios from 11 May 2001 (SD31) and 19 September 2001 (SD32). For the model validation simulations, all the model parameters in the calibrated models, including hydrodynamic conditions, copper loadings, settling velocities, and partitioning coefficients, remained unchanged. However, field data on DOC, TSS, pH, and salinity for 11 May 2001 (SD31) and 19 September 2001 (SD32) are used in the validation of the integrated CH3D/seawater-BLM model. As indicated above, these parameters are required input parameters for seawater-BLM. The expectation for the model validation is that once the model is calibrated adequately it should be able to predict the F&T of copper using a minimal set of site-

specific data. The procedure for the validation includes prediction for each validation scenario, 11 May 2001 (SD31) and 19 September 2001 (SD32), with the general characteristics from the four calibration scenarios, 30 August 2000 (SD26), 30 January 2001 (SD27), 27 February 2002 (SD33), and 14 May 2002 (SD35). The results from the validation are four sets of copper distributions for each calibration scenario.

11 May 2001 (SD31). There was a general tendency to under-predict Cu_{tot} at the mouth of the bay, and to over-predict those concentrations in the back of the bay. Measured Cu_{tot} on 11 May 2001 (SD23) show an almost constant increase from the mouth to box 23, with almost constant values in boxes 24 to 27 in the back of the bay (Figure 61). The tendency to under-predict Cu_{tot} in the area influenced by coastal waters and to over-predict in the back of the bay resulted in slopes larger than one for the comparisons between predicted and measured values for 30 August 2000 (SD26), 27 February 2002 (SD33), and 14 May 2002 (SD35), as shown in Figure 62. The validation for this simplest case of Cu_{tot} distribution is within the performance criteria, with predicted values explaining from 74 to 90% of the variance of the measured values (Figure 62, Table 14).

Predictive parameters from a scenario with similar conditions must be applied. Application of parameters developed in the calibration for 30 January 2001 (SD27) grossly under-predicted the Cu_{tot} measured on 11 May 2001 (SD31) (Figure 61 and Figure 62). Conditions on 30 January 2001 (SD27) in San Diego Bay were extremely different in comparison with the other sampling dates, which is most obvious in the distribution of TSS; TSS measured on 30 January 2001 (SD27) were the lowest concentrations measured of the six sampling events (Figure 63). Calibration under these conditions directed towards applying the largest settling velocity of the four calibration events (19.5 cm hr^{-1}), as shown in Table 10. Application of these extreme characteristics was unjustified for the validation with the 11 May 2001 (SD31) or the 19 September 2001 (SD32) measured data, as these scenarios do not have the same characteristics as those from 30 January 2001 (SD27).

Predicted Cu_{diss} for 11 May 2001 (SD31) provided similar results to Cu_{tot} prediction. In general, predicted values have better agreement to measured data for the area of the bay influenced by tidal flushing (Figure 64). However, the model throughout the bay underestimated Cu_{diss} by 0.3 to 0.6 µg L^{-1}, although the measured values are within the ranges predicted by the model for most of the bay, except the inner bay. The predicted values explain between 77 to 92% of the variance of measured values (Figure 65, Table 14). Similar to Cu_{tot} validation, the parameters from 30 January 2001 (SD27) grossly under-estimated the measured Cu_{diss}.

Cu^{2+} concentrations have good agreement with the measured data. Predicted Cu^{2+} (pCu) are in the same order of magnitude as the values measured on 11 May 2001 (SD31) (Figure 66). Out of 96 predicted mean daily values, only two (2%) are more than one order of magnitude different from the measured values. Both of these differences were observed in box 5, which always had a decrease in Cu^{2+} concentration (Figure 64). As in the calibration effort, Cu^{2+} concentrations were under-estimated in the mouth of the bay (boxes 2 and 3), but predicted values were very reasonable within the bay. The increase in Cu^{2+} in the inner part of the bay (boxes 25 to 27) is exaggerated by the predicted values (Figure 66). In contrast to the results for the validation for Cu_{tot} and Cu_{diss}, Cu^{2+} values predicted with the parameters from the 30 January 2001 (SD27) scenario are in the same order of magnitude as the measured data.

19 September 2001 (SD32). This event is a more complex case for validation than the previous one. The distribution of Cu_{tot} measured on 19 September 2001 (SD32) shows an almost constant and low value of about 0.4 µg L^{-1} for boxes 1 to 7 (area influenced by coastal waters). Going into the bay, it increases up to 0.96 µg L^{-1} by box 11, with a doubling in concentration (1.98 µg L^{-1}) going to box 12, a relatively small increase to box 17 (2.28 µg L^{-1}), and stepper increase to box 20 (2.94 µg L^{-1}). From

box 20 to the back of the Bay the concentration distribution is erratic, with most of the concentrations following an increase pattern to about 3.5 µg L^{-1} in boxes 25 and 26, and boxes 24 and 27 having concentrations of around 2.7 µg L^{-1} (Figure 67). The complexity of the concentration distribution resulted in a somewhat lower capability for prediction. The low concentration measured in boxes 2 to 7 is probably the hardest feature to predict, with different scenarios being more able to predict the distributions in the middle or the back of the bay. Three scenarios predicted the step-increase in concentration. The distribution of measured values resulted in two groups of data for the comparison with predicted ones (Figure 68), with each group following a different tendency. However, this comparison indicates that the capability for prediction is within performance criteria, with predicted values explaining from 74 to 86% of the variance of the measured values (Figure 69, Table 14).

Prediction of Cu_{diss} distributions for 19 September 2001 (SD32) had similar results to prediction of Cu_{tot} distributions. Three of the scenarios were unable to predict the low concentrations by the mouth of the bay, but could predict the sharp increase in concentration measured between boxes 11 and 12 (Figure 69). The integrated CH3D/seawater-BLM model produced values that are within the performance criteria, with predicted values explaining from 68 to 80% of the variance of measured values (Figure 70, Table 14).

Predicted Cu^{2+} concentrations are within an order of magnitude of the measured values (Figure 71). Similar to the calibration scenarios and the other validation scenario, the integrated model predicted mean Cu^{2+} concentrations as more than one order of magnitude different in the mouth of the bay (box 2), and values within an order of magnitude of the measured ones for the rest of the bay (Figure 71).

For both calibration and validation, 97% of the predicted values are within one order of magnitude of the measured Cu^{2+} (Figure 72), which fulfills the performance criteria for the prediction of Cu^{2+} in San Diego Bay.

In general, validation of the integrated model was within performance criteria for Cu_{tot} and Cu_{diss} (Table 14). The variance of the measured Cu_{tot} is in a range of 74 to 90% for the eight validation cases, and from 68 to 92% for Cu_{diss}. All the 16 different cases analyzed are within the performance criteria.

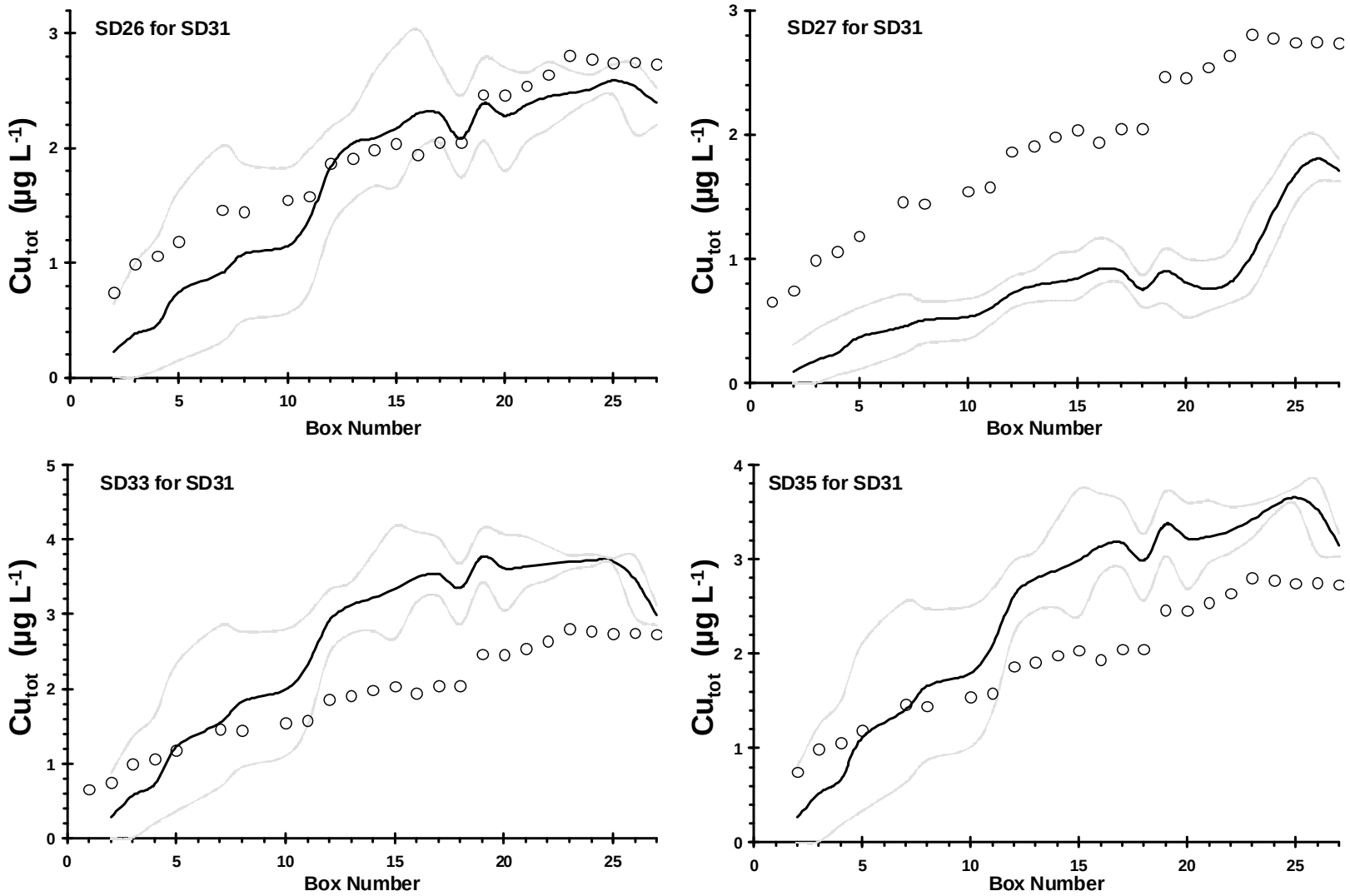


Figure 61. Validation of Cu_{tot} (µg L^{-1}) using parameters from four calibrated scenarios to predict data measured on 11 May 2001 (SD31).

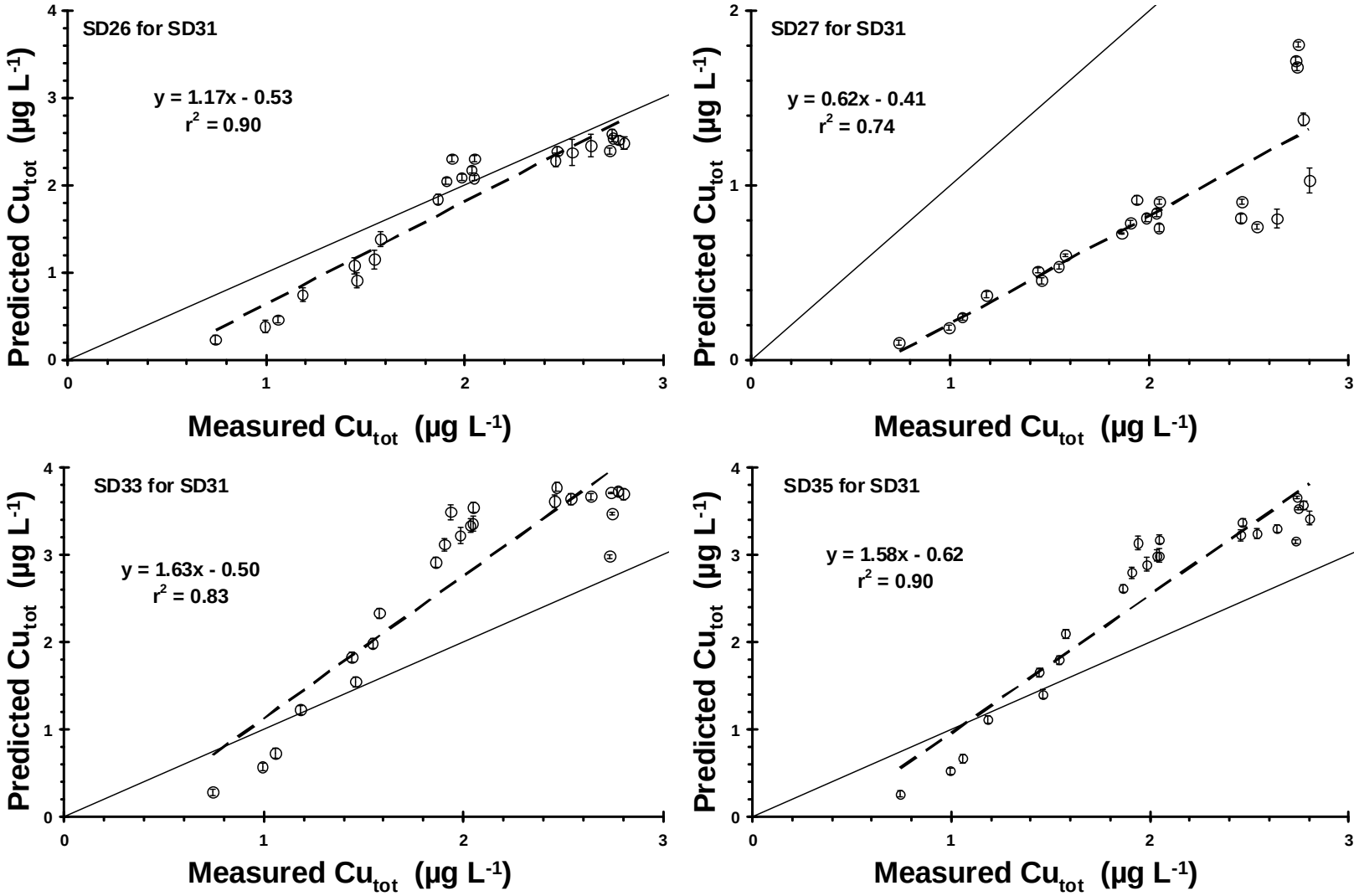


Figure 62. Comparisons between predicted and measured Cu_{tot} (µg L^{-1}) for the validation of the integrated model with the data from 11 May 2001 (SD31).

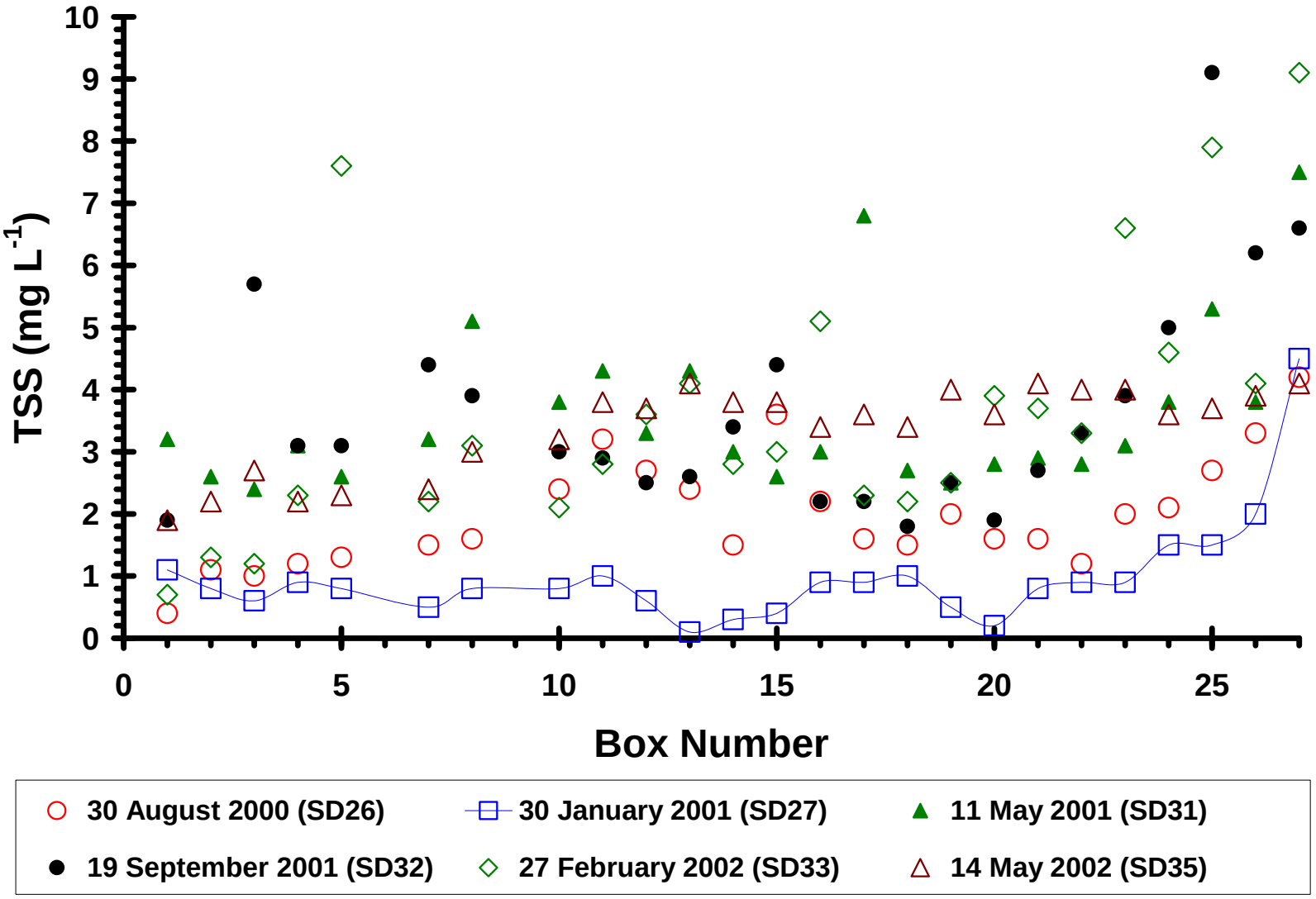


Figure 63. Distributions of TSS (mg L^{-1}) in San Diego Bay measured as part of project SERDP CP-1156.

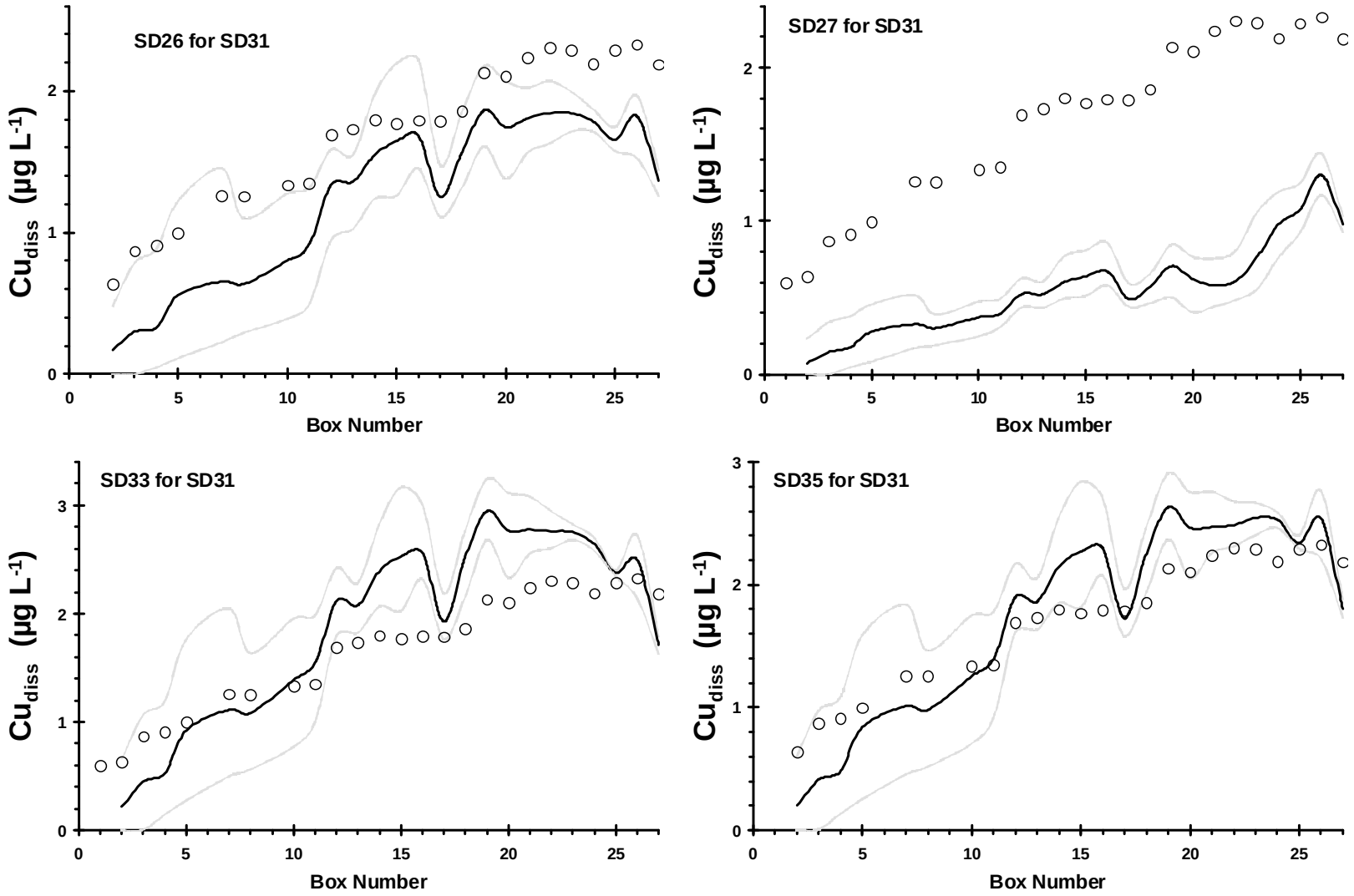


Figure 64. Validation of Cu_{diss} (µg L^{-1}) using parameters from four calibrated scenarios to predict data measured on 11 May 2001 (SD31).

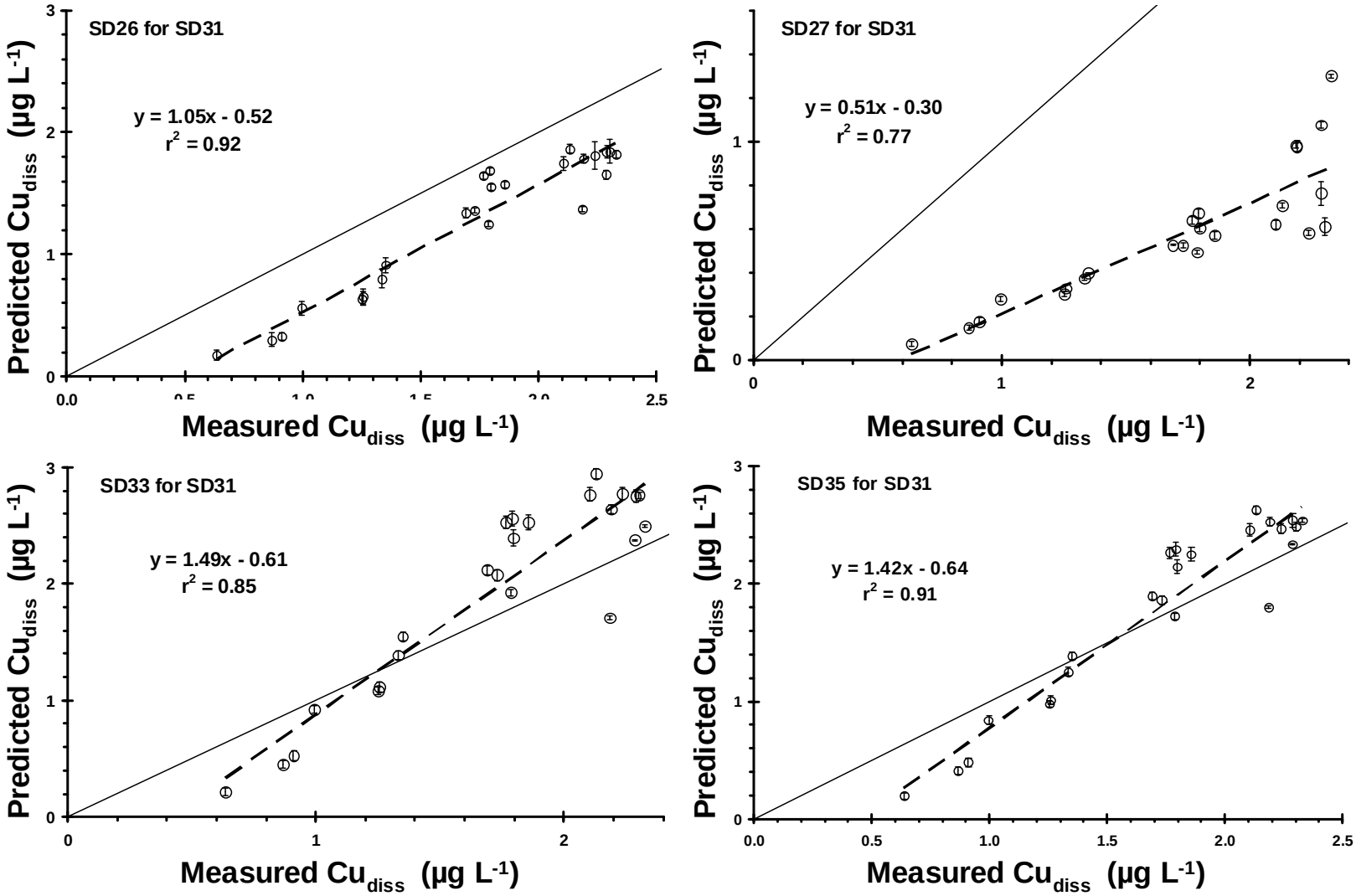


Figure 65. Comparisons between predicted and measured Cu_{diss} (µg L^{-1}) for the validation of the integrated model with the data from 11 May 2001 (SD31).

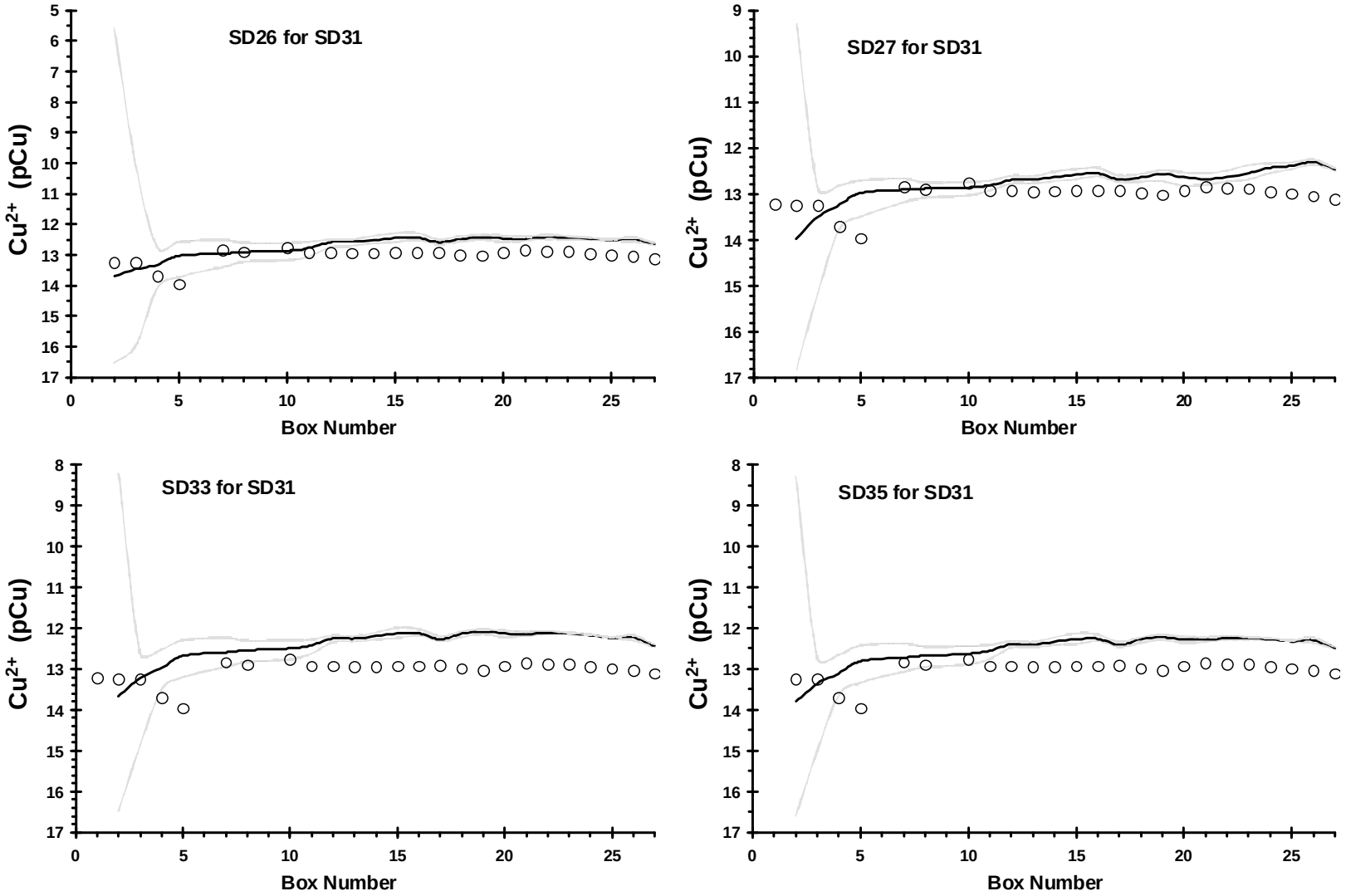


Figure 66. Validation of Cu^{2+} (pCu) using parameters from four calibrated scenarios to predict data measured on 11 May 2001 (SD31).

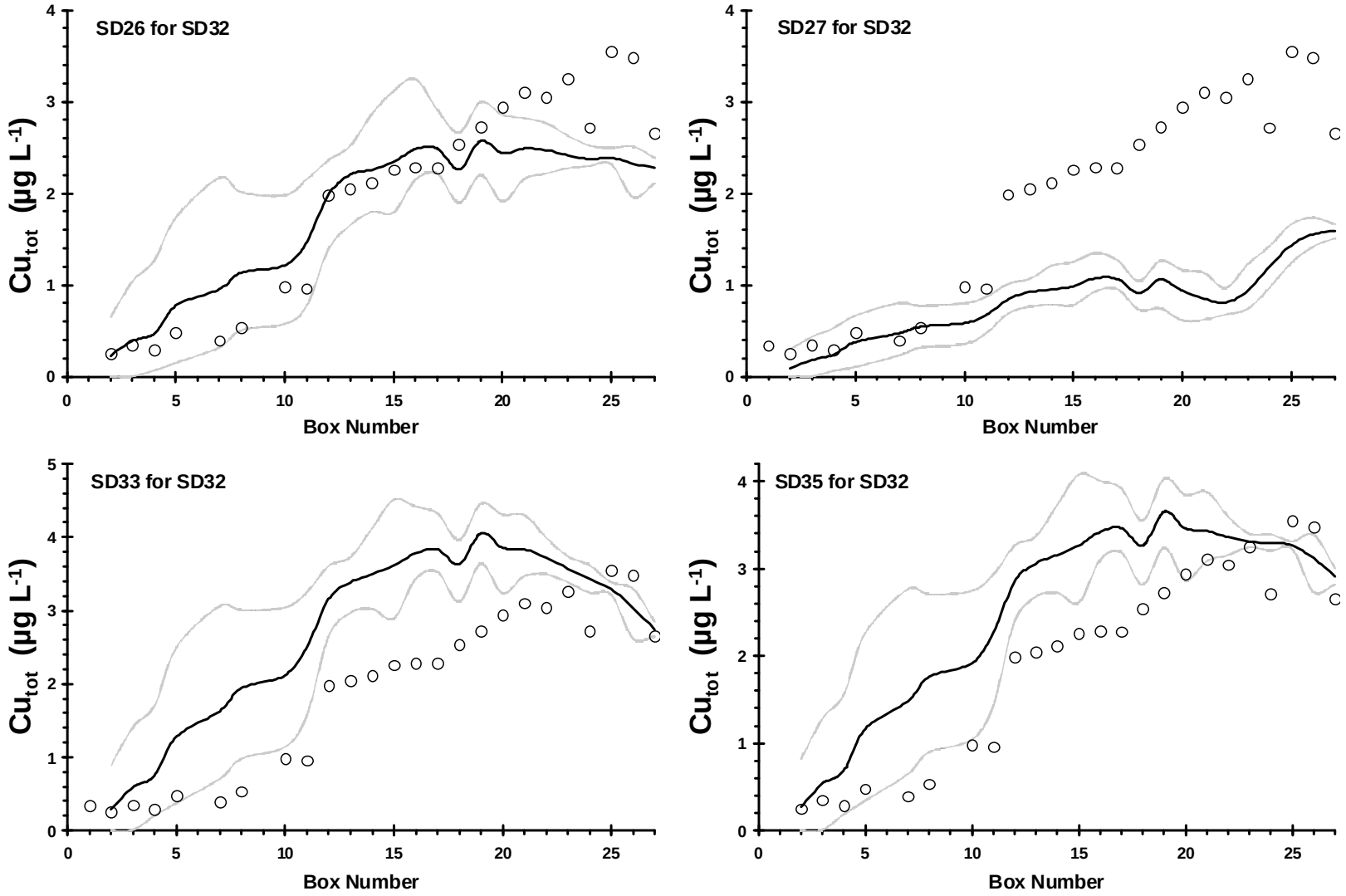


Figure 67. Validation of Cu_{tot} (µg L^{-1}) using parameters from four calibrated scenarios to predict data measured on 19 September 2001 (SD32).

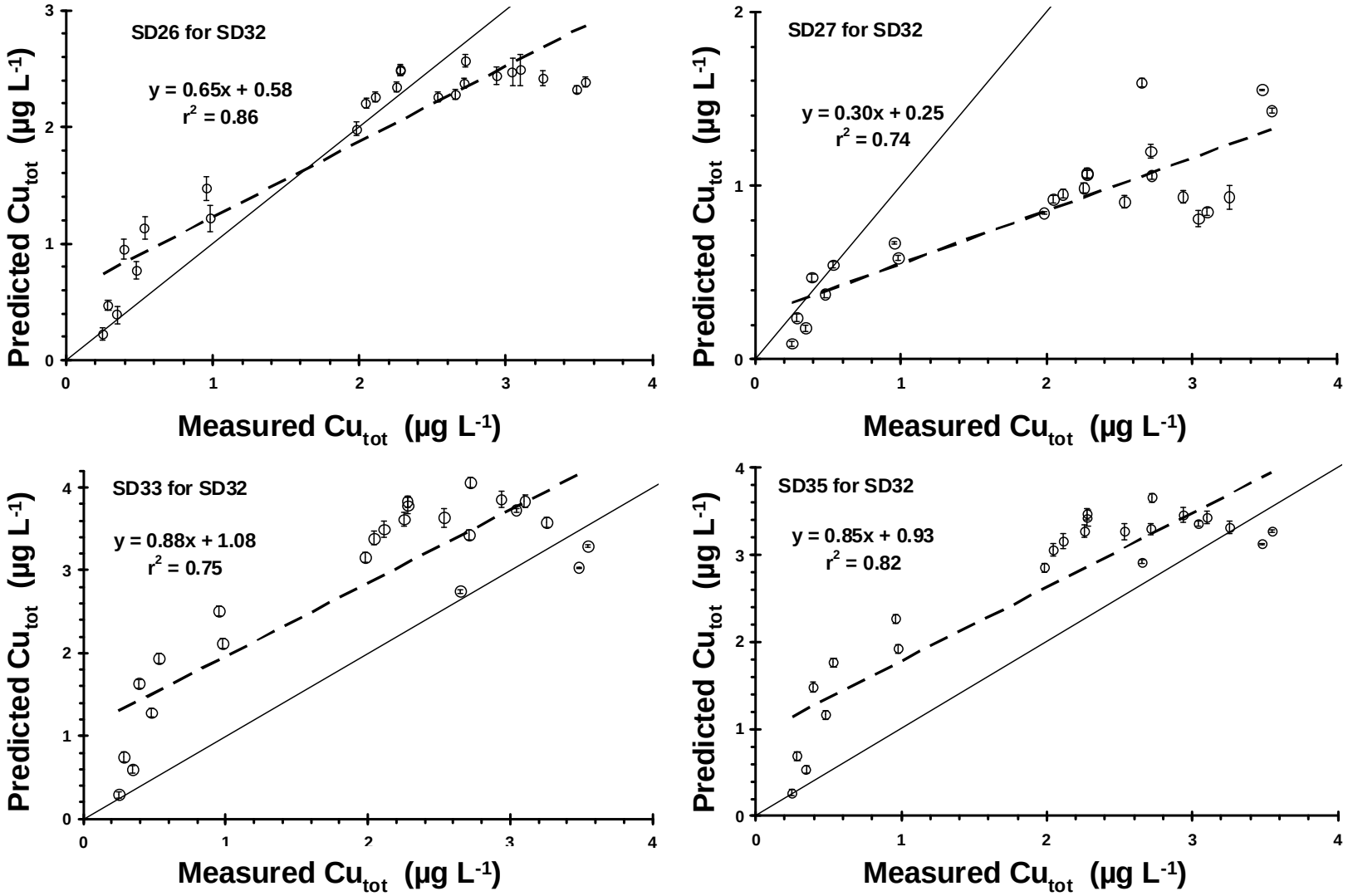


Figure 68. Comparisons between predicted and measured Cu_{tot} (µg L^{-1}) for the validation of the integrated model with the data from 19 September 2001 (SD32).

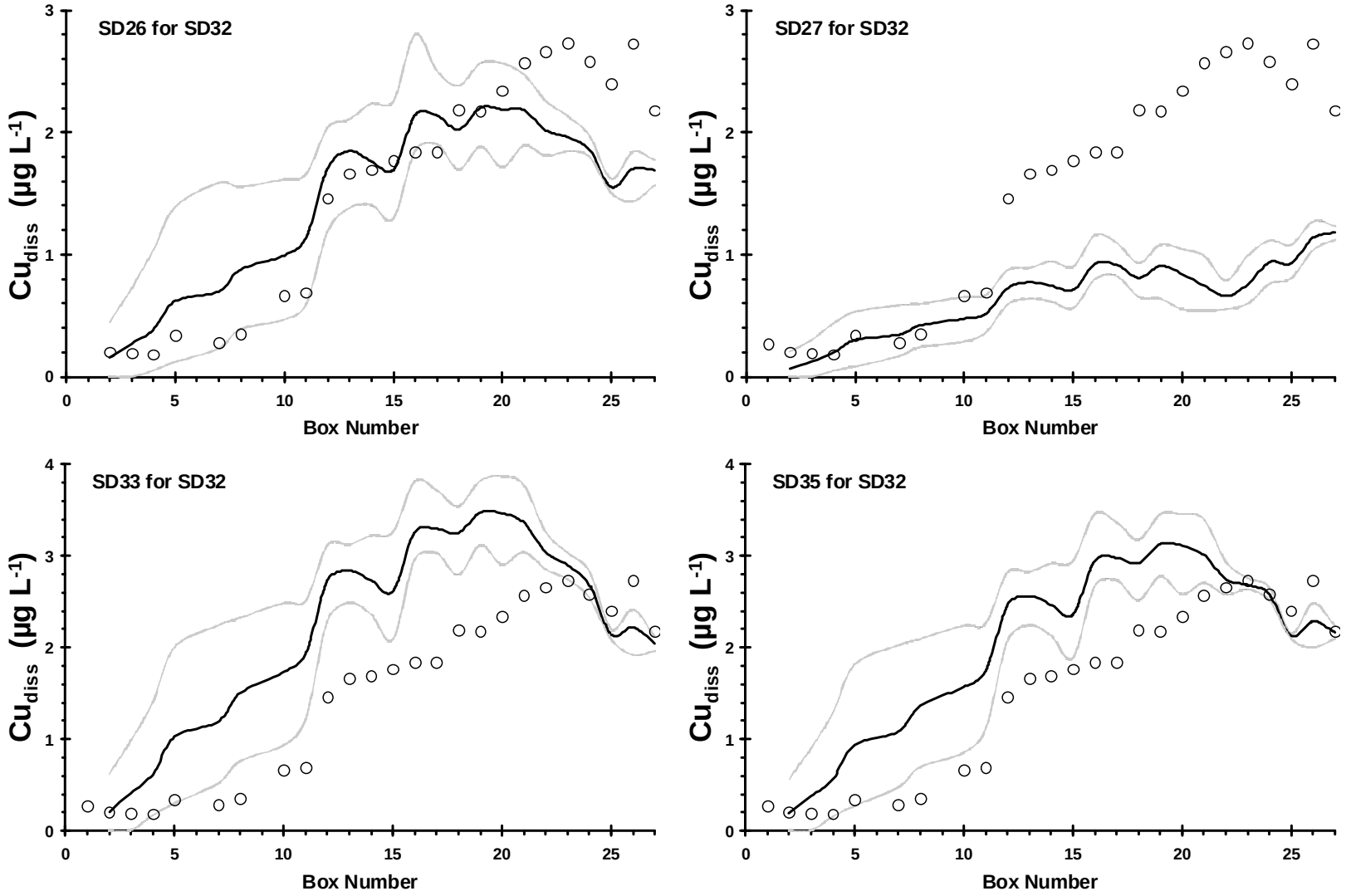


Figure 69. Validation of Cu_{diss} (µg L^{-1}) using parameters from four calibrated scenarios to predict data measured on 19 September 2001 (SD32).

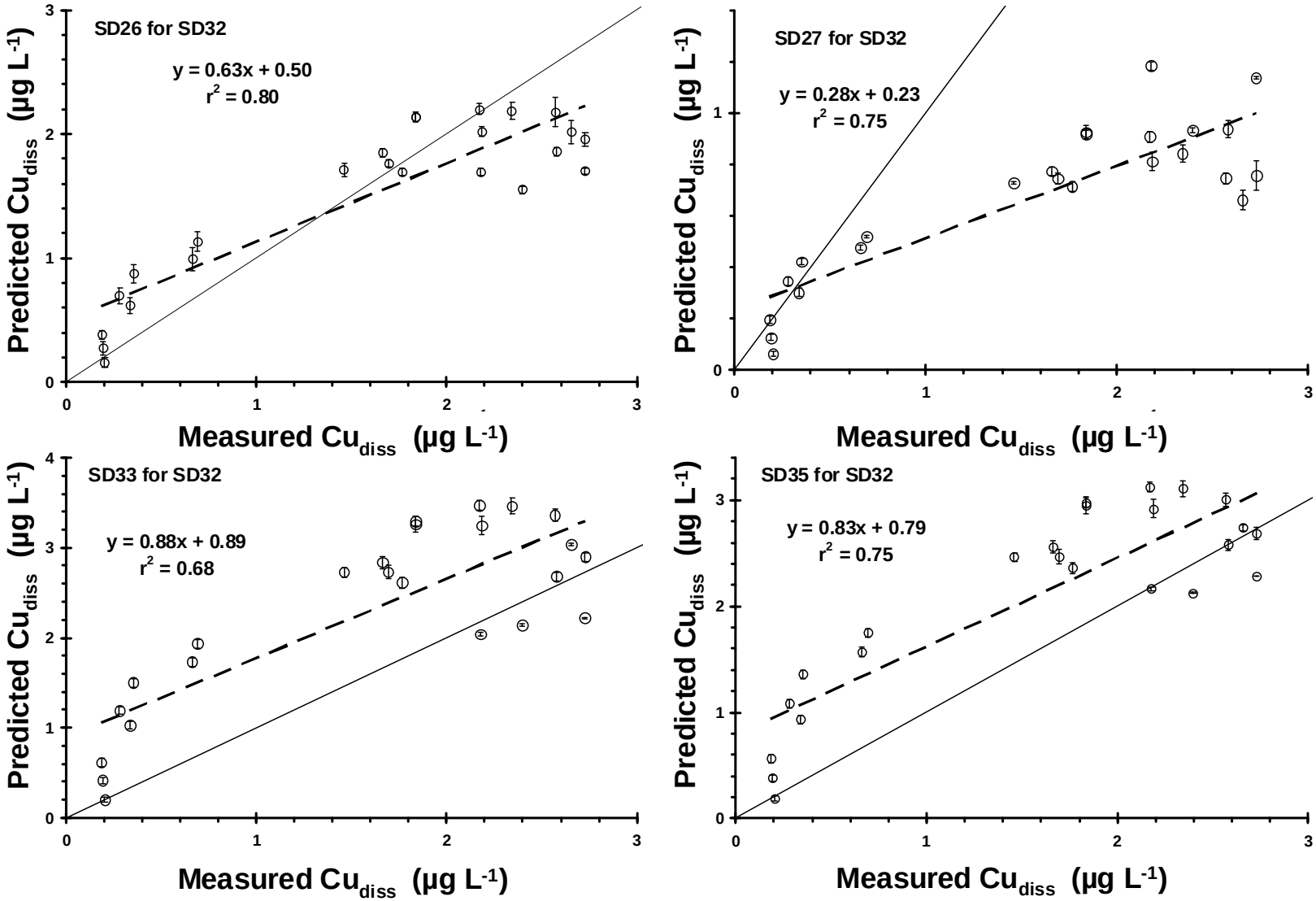


Figure 70. Comparisons between predicted and measured Cu_{diss} (µg L^{-1}) for the validation of the integrated model with the data from 19 September 2001 (SD32).

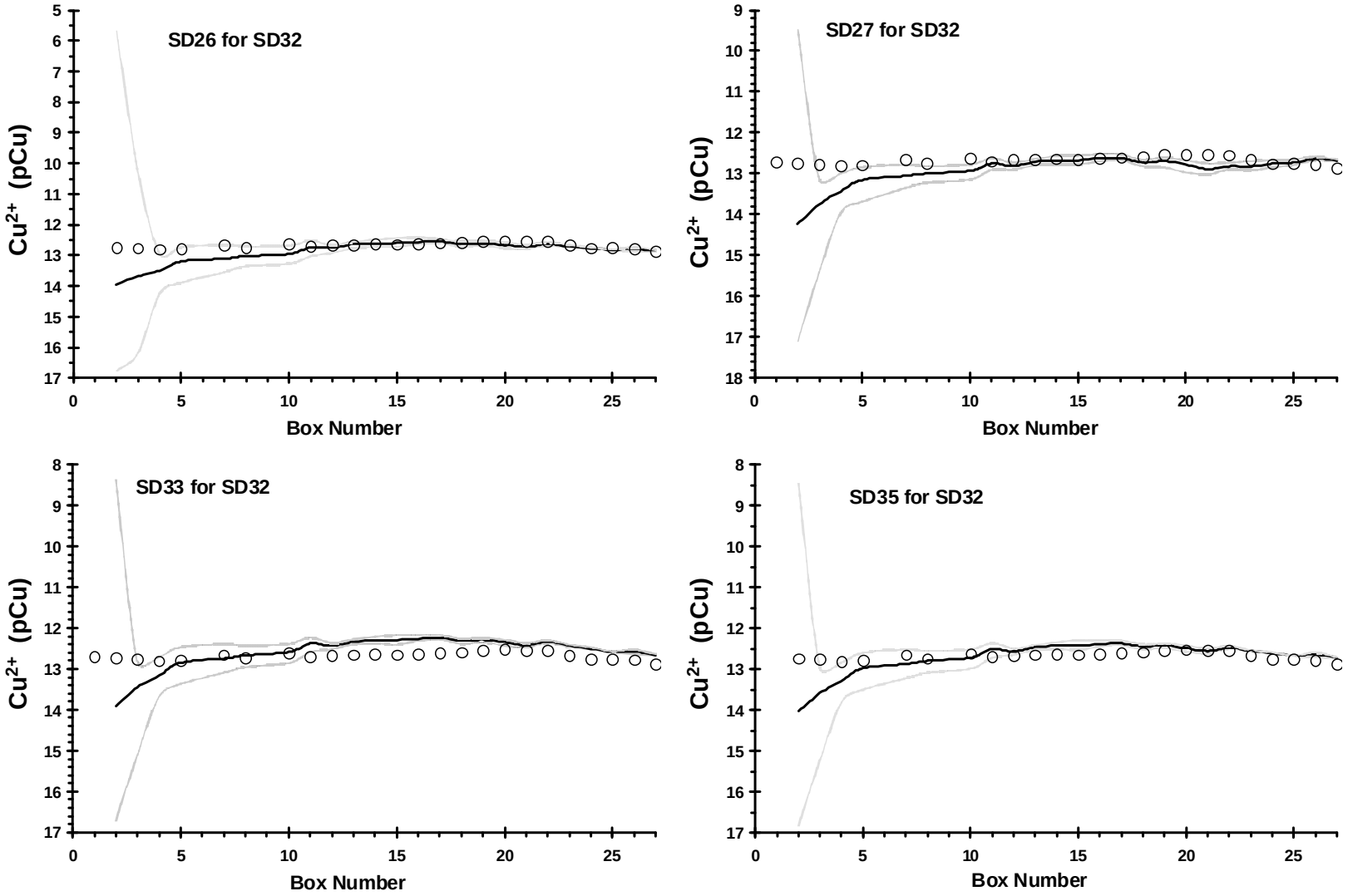


Figure 71. Validation of free copper ion (Cu^{2+}, pCu) using parameters from four calibrated scenarios to predict data measured on 19 September 2001 (SD32).

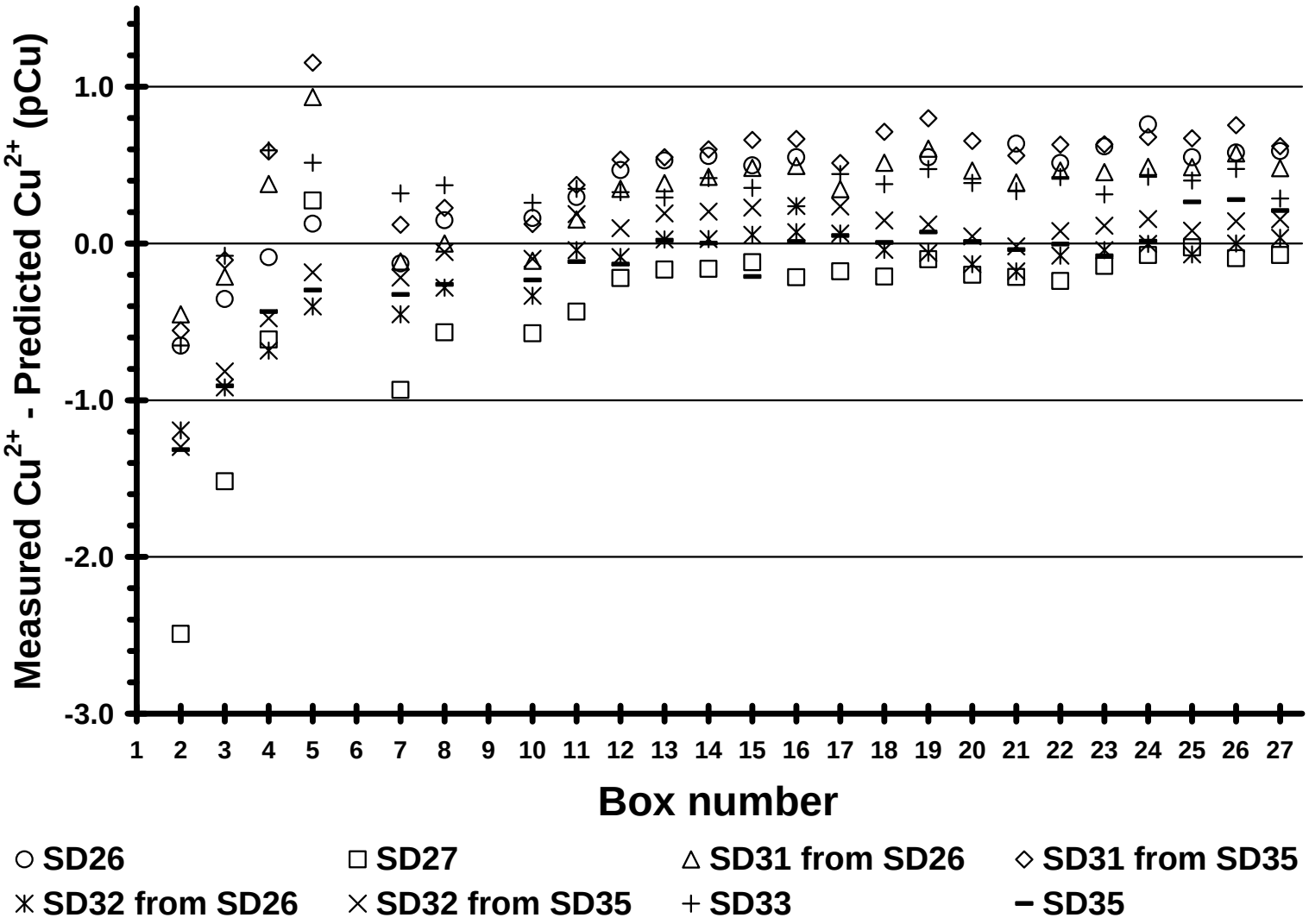


Figure 72. Difference between measured and predicted Cu^{2+} (pCu) for the calibration and validation in San Diego Bay, 97% of the predicted values are within one order of magnitude of the measured values.

Table 14. Statistics for validation of the integrated model in San Diego Bay

Validation event	Sampling date	Cu_{tot}			Cu_{diss}		
		% Variance	Intercept	Slope	% Variance	Intercept	Slope
11 May 2001 (SD31)	30 August 2000 (SD26)	90	-0.53	1.17	92	-0.52	1.05
	30 January 2001 (SD27)	74	-0.41	0.62	77	-0.30	0.51
	27 February 2002 (SD33)	83	-0.50	1.63	85	-0.61	1.49
	14 May 2002 (SD35)	90	-0.62	1.58	91	-0.64	1.42
19 September 2001 (SD32))	30 August 2000 (SD26)	86	0.58	0.65	80	0.50	0.63
	30 January 2001 (SD27)	74	0.25	0.30	75	0.23	0.28
	27 February 2002 (SD33)	75	1.08	0.88	68	0.89	0.88
	14 May 2002 (SD35)	82	0.93	0.85	75	0.79	0.83

4.3.13 D Validation of Integrated CH3D/Seawater-BLM Model Pearl Harbor

The models calibrated for 15–18 March 2005 (Event 1) and 15–19 May 2006 (Event 4) were used for model validation of the data for 18–20 October 2005 (Event 2). In general, these three sampling events are similar since they all are outside of the wet season with no noticeable difference in the loading or hydrodynamic conditions. All the model parameters, including the hydrodynamics, copper loads, and settling velocities calibrated for these events were used during the model validation. The only event-specific data used for model validation were TOC, DOC, TSS, and pH measured during 18–20 October 2005 (Event 2). Therefore, two sets of model validation results were obtained, one from the calibrated 15–18 March 2005 (Event 1) model and the other from the calibrated 15–19 May 2006 (Event 4) model.

Comparison between predicted and measured Cu_{tot} and Cu_{diss} for the two validation models are provided in Figure 73 and Figure 74. While the calibrated models can predict 72% or better of the variance in the measured Cu_{tot}, they can only predict 40% or better the variance in the measured Cu_{diss} (Table 15). In these cases, the correlation between predicted and measured values is highly affected by the value measured at South Station (Cu_{tot} 0.54 µg L^{-1}, Cu_{diss} 0.53 µg L^{-1}) that is predicted at a much lower concentration (0.20 µg L^{-1} for Cu_{tot} and Cu_{diss}). The position of this data point with respect to the rest of the information is suspect for the Cu_{diss} plot. While this data point agrees with the trend for Cu_{tot}, where the prediction capability is within performance criteria, it does not follow the trend for Cu_{diss}, where the criteria fail. As the overall measured Cu_{diss} is 71.2% of the measured Cu_{tot} in Pearl Harbor (Figure 75), the Cu_{diss} concentration for South Bay could be assumed to be 0.38 µg L^{-1} instead of the measured 0.53 µg L^{-1}. This assumed value is within the precision of the measurements, and application of this concentration will indicate that the integrated model could predict 89% or better of the variance of the measured Cu_{diss} values. This analysis supports the finding on the effect of the concentration range on the predictive capability of the integrated model. The example here is striking in the sense that just one value could affect this capability. These results also attest to the importance on the number of data points available for modeling, with the limited number of data points for Pearl Harbor also affecting the capability of the modeling effort. Figure 76 shows the Cu_{tot} concentration contours predicted by the integrated model for Pearl Harbor. Overall, Cu_{tot} are low (i.e., less than 1 µg L^{-1}) for most of the regions, except in regions near the freshwater stream discharges and the Naval Submarine Base, where predicted Cu_{tot} attain values as high as 2–3 µg L^{-1}.

Application of the integrated CH3D/seawater-BLM to Pearl Harbor resulted in reasonable predictions of Cu^{2+} concentration (Figure 77 and Figure 78). The predicted Cu^{2+} (pCu) values are just below 13 for almost all the regions except at the South location, where simulated Cu^{2+} reaches 13. However, there was a slight positive bias in BLM predictions. Variability in measured Cu^{2+} concentration not related to DOC was similar in magnitude to that seen in San Diego data (Figure 15). Most predictions (83%) were within a factor of five of the reported values, but only 44% were within a factor of two. However, no measured Cu^{2+} data are available for comparison with model results.

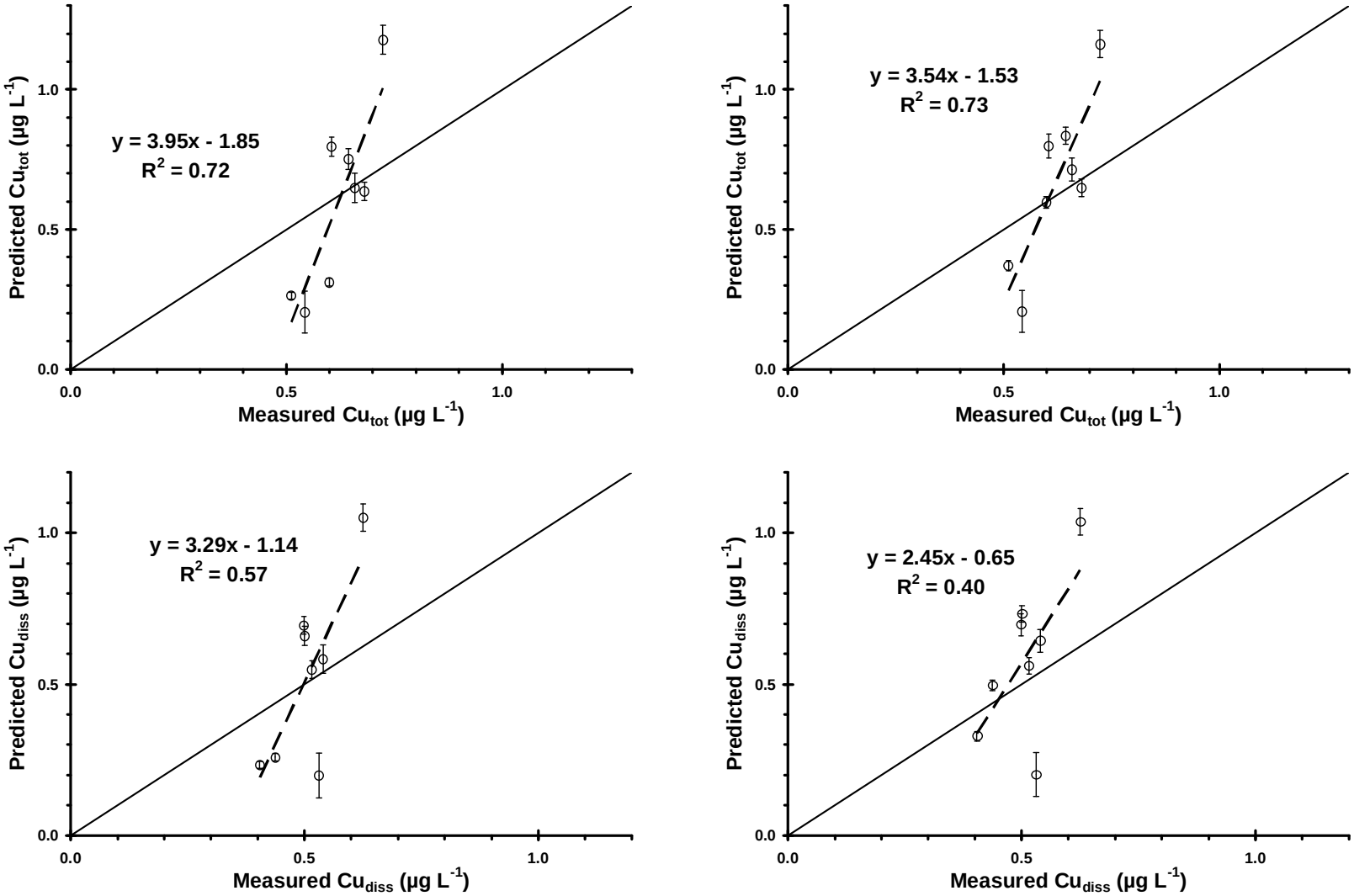


Figure 73. Predicted versus measured Cu_{tot} (top) and Cu_{diss} (bottom) for 18–20 October 2005 (Event 2) using calibrated model for 15–18 March 2005 (Event 1) (left) and for 15–19 May 2006 (Event 4) (right).

Table 15. Statistics for the validation of the integrated CH3D/seawater-BLM model in Pearl Harbor

Validation Event	Sampling date	Cu_{tot}			Cu_{diss}		
		% Variance	Intercept	Slope	% Variance	Intercept	Slope
18-20 October 2005 (Event 2)	15–18 March 2005 (Event 1)	72	-1.85	3.95	57	-1.14	3.29
	15-19 May 2006 (Event 4)	73	-1.53	3.54	40	-0.65	2.45

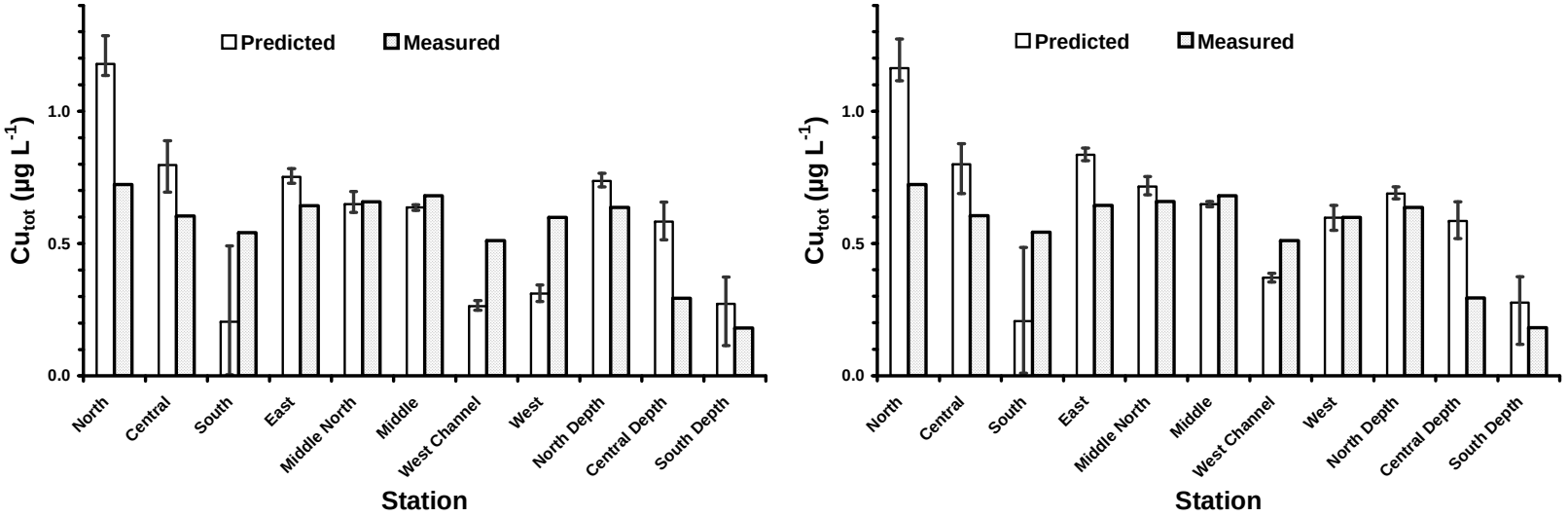


Figure 74. Comparison between predicted and measured Cu_{tot} for 18–20 October 2005 (Event 2) with parameters from 15–18 March 2005 (Event 1) (left) and 15–19 May 2006 (Event 4) (right).

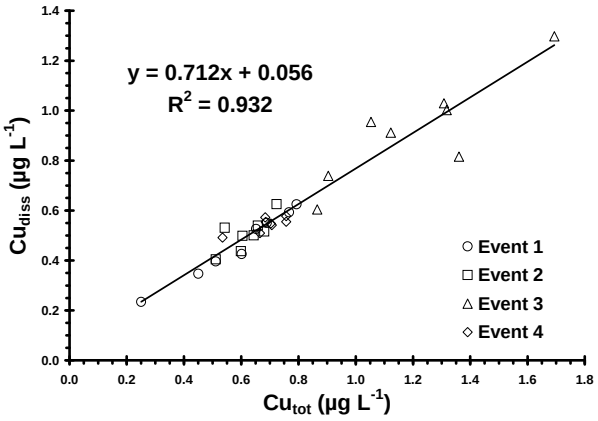


Figure 75. Relationship of Cu_{diss} to Cu_{tot} measured in ambient waters of Pearl Harbor by Earley et al. (2007). In general, 71.2% of the copper is in the dissolved fraction.

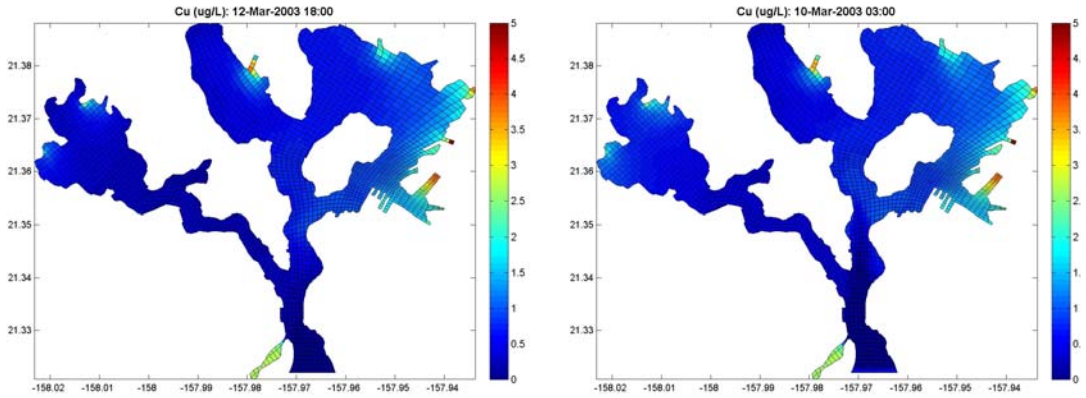


Figure 76. Predicted Cu_{tot} contours from the integrated model for 18–20 October 2005 (Event 2), using calibrated model for 15–18 March 2005 (Event 1) (left) and 15–19 May 2006 (Event 4) (right).

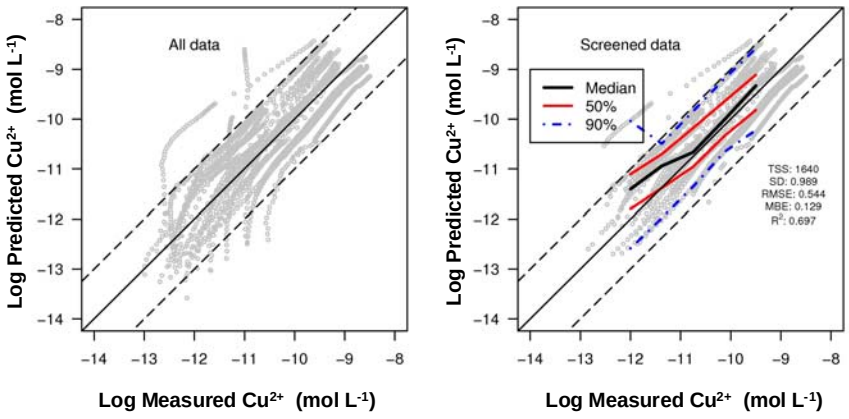


Figure 77. Comparison between predicted and measured Cu^{2+} in Pearl Harbor. Statistical data and linear delimitations are same as in Figure 16.

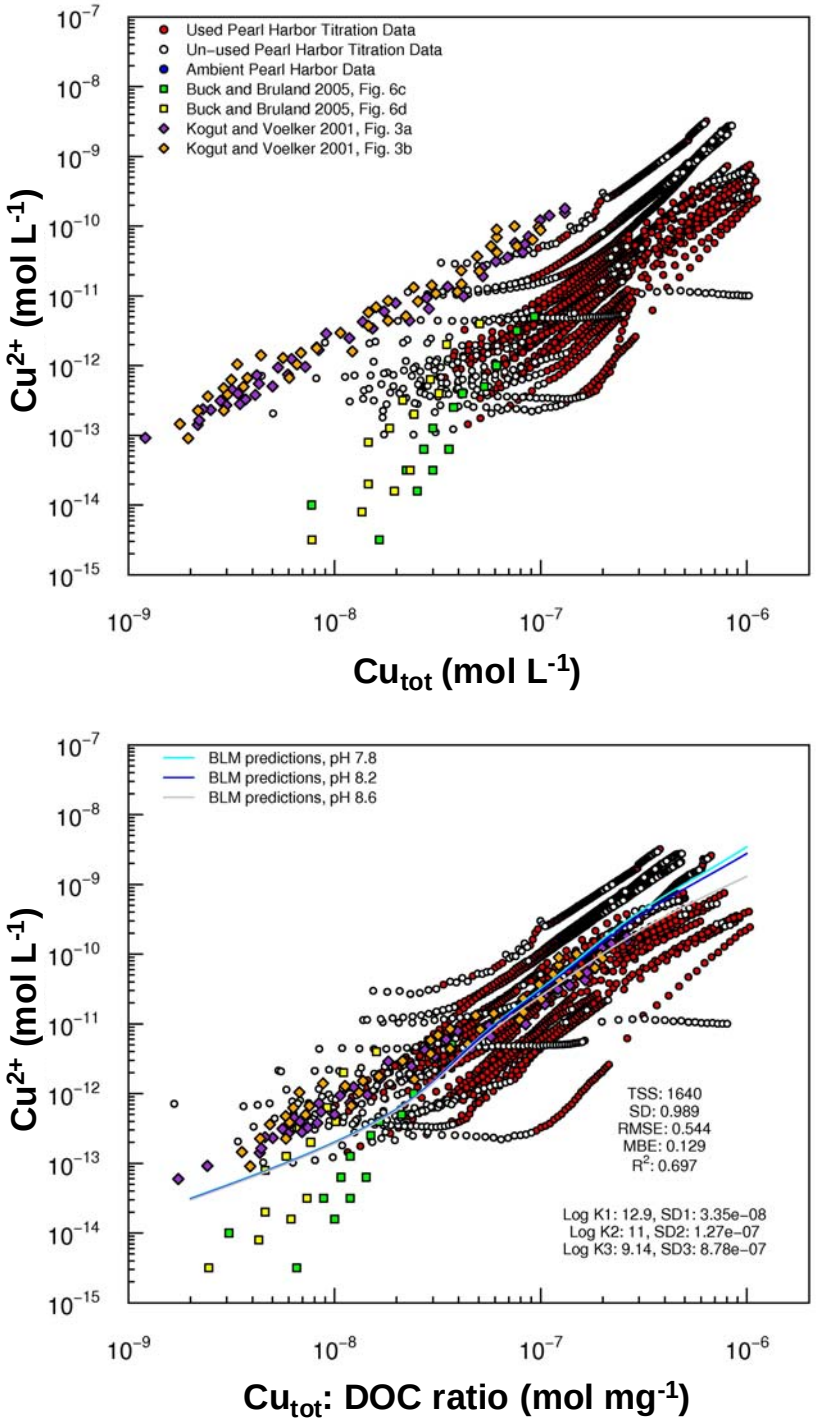


Figure 78. Application of the calibrated seawater-BLM Cu speciation model to the whole Pearl Harbor data set. For comparison, results from Kogut and Voelker (2001) and Buck and Bruland (2005) are included.

4.3.14 Integrated Model: CH3D/Seawater-BLM Prediction of Toxicity and WER

One of the advantages of the integrated CH3D/seawater-BLM model is the prediction of high-resolution spatial distributions of parameters of regulatory concern, including toxicity threshold (EC50, µg L^{-1}) and WER. The lethal level accumulations (LA50) for bay mussel (*M. galloprovincialis*), sand dollar (*D. excentricus*), purple sea urchin (*S. purpuratus*) and oyster (*C. gigas*) that were calibrated for the model (Section 4.3.2 D, Table 9) were used for the validation in the prediction of toxicity for Pearl Harbor. Application of the model to Pearl Harbor toxicity data resulted in reasonable predictions for the three organisms tested (Figure 79). Note that the model for *C. gigas* was calibrated to the Pearl Harbor data (no toxicity tests were conducted with *C. gigas* in San Diego Bay). For the other organisms, this application serves as a validation of the complete seawater-BLM. The toxicity data for Pearl Harbor showed a much smaller range in EC50 values, and this is likely because of the smaller range in bioavailability factors (i.e., primarily DOC). For all three organisms, all predictions were within a factor of five of reported EC50s. For *M. galloprovincialis*, 87% of predictions were within a factor of two of reported values, while this number was 92 and 100% for *C. gigas* and *S. purpuratus*, respectively. EC50s from Pearl Harbor did not show a clear response to DOC for any of the three organisms tested (Figure 79).

A comparison of measured and predicted EC50s for all the data from San Diego and Pearl Harbor is shown in Figure 80. For *M. galloprovincialis*, 83% of the observations were within a factor of two of reported values. For *C. gigas*, this value was 92%, while all predictions were within a factor of two of reported values for *S. purpuratus* and *D. excentricus*. Examples of the high-resolution distributions of the toxicities predicted for three organisms for San Diego Bay in the validation cruise of 19 September 2001 (SD32) are given in Figure 81. These distributions attest to the capability of the integrated model to predict spatial distributions of parameters of regulatory interest at a high resolution (≈100 m) in the bay, which contrasts with the demanding effort required for measuring toxicity in enough samples to provide spatial distribution.

The predicted distributions of threshold toxicity values show the need to resolve spatial distributions of DOC. The spatial distributions of the toxicity threshold factor EC50 in Figure 81 show a gradient in its spatial distribution. These distributions are predicted by modeling DOC as having a spatially uniform production that gives average concentrations from the measurements. Therefore, the spatial distribution of DOC is averaged in the geographic regions in the bay. Further improvement in the resolution of DOC distributions will provide better refinement in the prediction of WQS.

The whole-body LA50 was used in conjunction with the data of TSS, DOC, pH, and salinity in the integrated model to derive predicted WER for San Diego Bay and Pearl Harbor. The reference water composition was taken as the mean of coastal samples from the Scripps Institute of Oceanography and from the University of California Davis Marine Pollution Studies Laboratory at Granite Canyon (a total of nine samples). WERs are shown for locations within San Diego Bay and Pearl Harbor in Figure 82. Geometric mean WERs were slightly higher for San Diego Bay than they were for Pearl Harbor (Table 16).

These calculated WER values are based on DOC measurements in the reference waters used in the toxicity tests, which averaged around 1.5 mg C L^{-1}. While this value may have been appropriate for comparison with those tests, it is somewhat higher than comparable reference waters. For example, in recent work for San Francisco Bay the DOC concentrations in Granite Canyon reference waters ranged from 0.3 to 0.8 mg L^{-1} (Arnold, Santore, and Cotsifas, 2005). For this application, if the WER values were based on BLM predictions using reference water with lower DOC concentrations, all of

the WER values would be higher, and it is unlikely that any would be below 1.0. The sensitivity of WER values to reference water chemistry is a clear disadvantage of the WER methodology, and the values shown below 1.0 should not be interpreted to mean that there are times when criteria values lower than the national ambient marine criterion would be appropriate.

The integrated CH3D/seawater-BLM model provides high-resolution prediction of WQS specific for the Bay. Cu_{diss} WERs are predicted at each box for each sampling cruise and for all the organisms. The geometric mean of these measurements is shown in Figure 82. In San Diego Bay, there is a gradient in the predicted WER going from values of about 1.4 by the mouth of the bay (boxes 2 to 11) to values around 2.0 in the back of the bay (boxes 23 to 26) and a maximum in box 27 (Figure 82). The geometric average Cu_{diss} WER for the bay is 1.479, which compares well with the range of 1.54 to 1.67 calculated by Rosen et al. (2005) for San Diego Bay.

Rosen et al. (2005) also measured a geographic distribution within the bay, with lower values (geometric mean 1.26) in the North Bay (boxes 1 to 17) and larger WERs (geometric mean 1.90) in the South Bay (boxes 18 to 27), similar to the distribution predicted by the integrated model (Figure 82). The integrated model predicts WERs with a geometric mean of 1.336 in the North and 1.761 in the South section of the bay. The comparison between predicted and measured Cu_{diss} WERs for the two DoD harbors (Figure 83) show that 88% of the values are within a factor of two of the measured values.

Implementation of WER predicted by the integrated CH3D/seawater-BLM model should provide regulatory relief while still achieving the level of protection intended by the WQC guidelines. Figure 84 shows the predicted levels of Cu_{diss}, the current WQC, and the level of relief provided by applying harbor-specific WQS in San Diego Bay. This figure also includes the Margin of Safety (MOS) predicted for the Bay. The MOS is the factor by which the predicted Cu_{diss} must be increased to reach threshold toxicity concentrations. The area affected by tidal flushing and inputs from the adjacent coastal waters provides more complexing capacity and dilution to the sources of copper, as indicated by MOS values between 7 in box 2 to 4.0 in box 10 (Figure 84). The natural complexation capacity and dilution of the inputs provides a MOS value of 2.2 ±0.5 for the rest of the bay. These results attest to the importance of adopting the integrated model for designation of environmental quality regulations, as it provides high-resolution geographic distributions of WQS and other important regulatory factors. It also shows that ambient copper concentrations are close to current marine WQC of 3.1 µg $L^{-}1$. If the marine WQC were to be lowered as was suggested in the 2003 draft U.S. EPA copper criteria document that proposed a value of 1.9 (U.S. EPA, 2003), then San Diego Bay would probably be listed as impaired due to copper concentrations. However, when bioavailability is considered in the development of site-specific criteria in the bay, the current copper concentrations are well below the criteria values with a margin of safety of at least 2× throughout the bay.

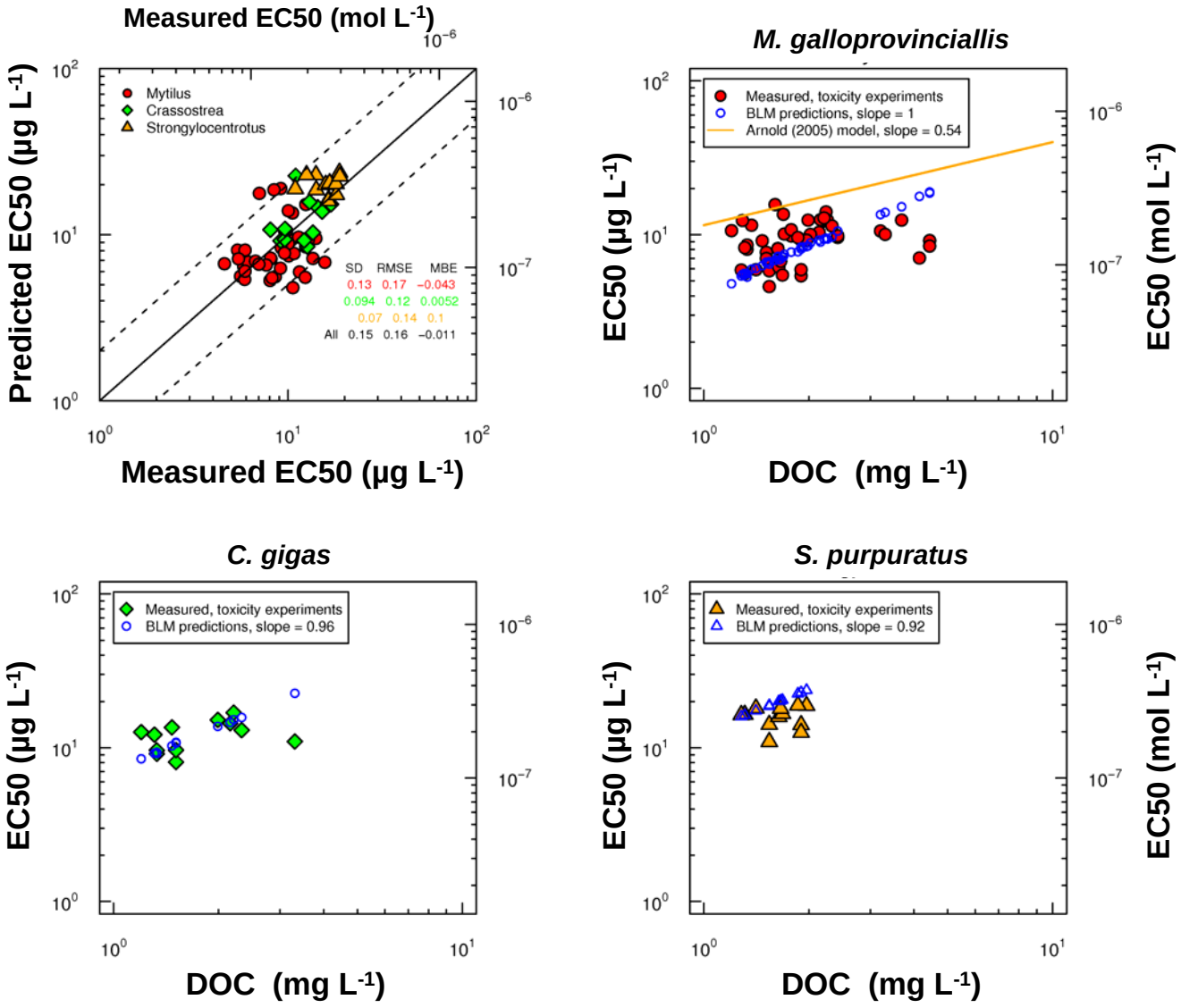


Figure 79. Measured and predicted Cu_{diss} EC50s for Pearl Harbor.

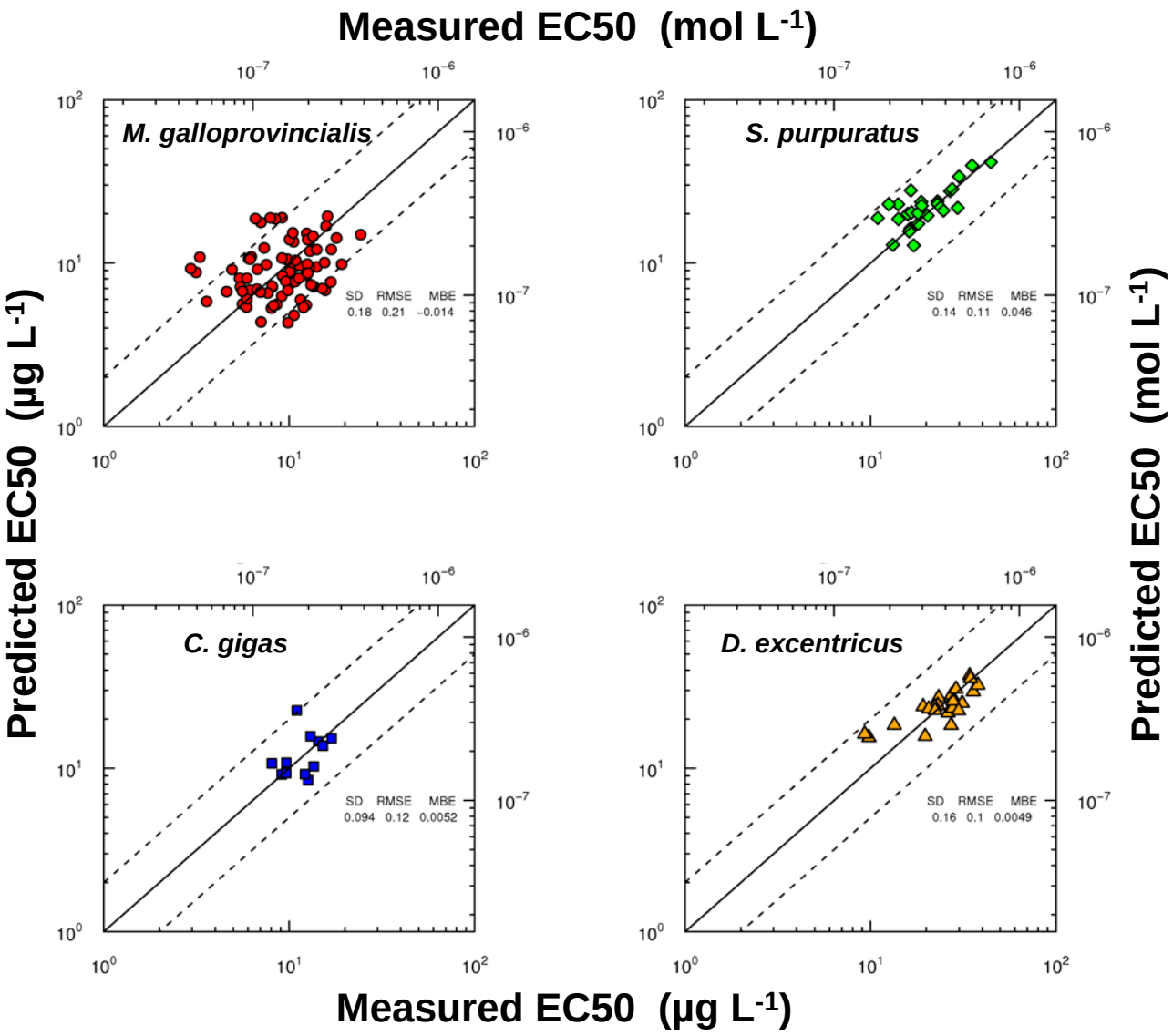


Figure 80. Measured and predicted Cu_{diss} EC50s for San Diego Bay and Pearl Harbor.

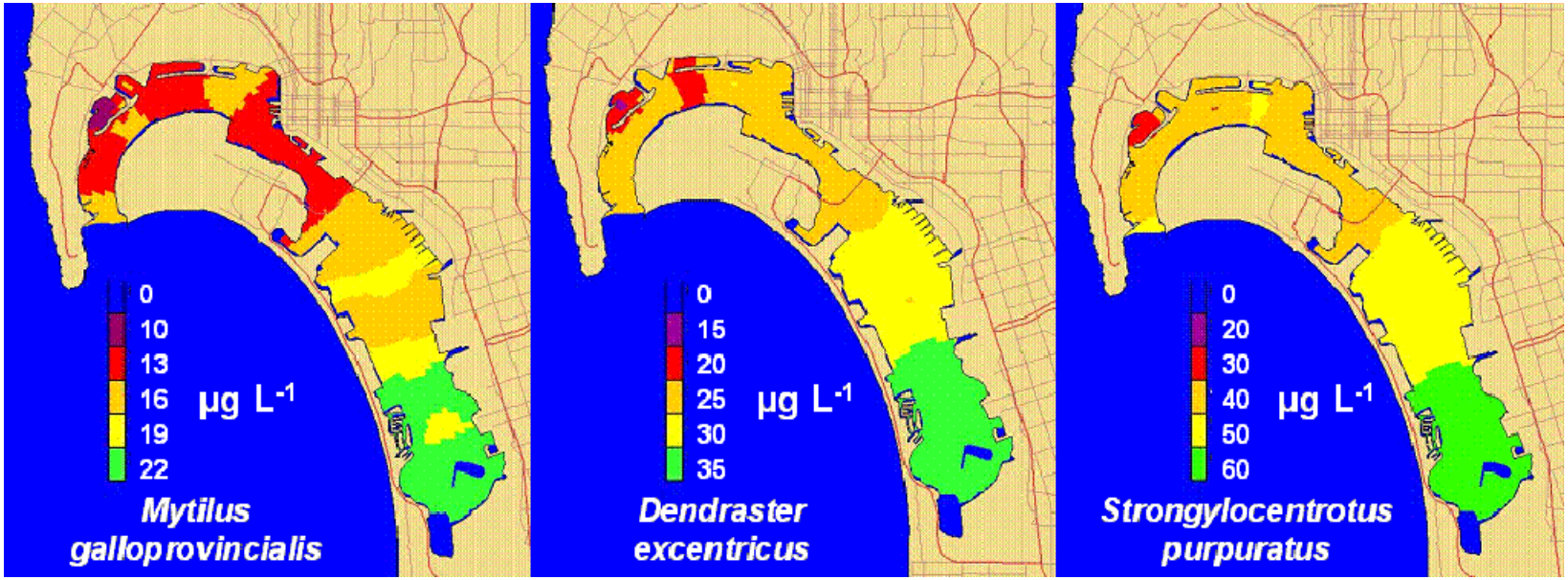


Figure 81. Spatial distribution of EC50 (toxicity threshold, µg L^{-1}) predicted for *M. galloprovincialis* (bay mussel), *D. excentricus* (sand dollar) and *S. purpuratus* (purple sea urchin) by the integrated CH3D/seawater-BLM model for the validation scenario of 19 September 2001 (SD32) in San Diego Bay.

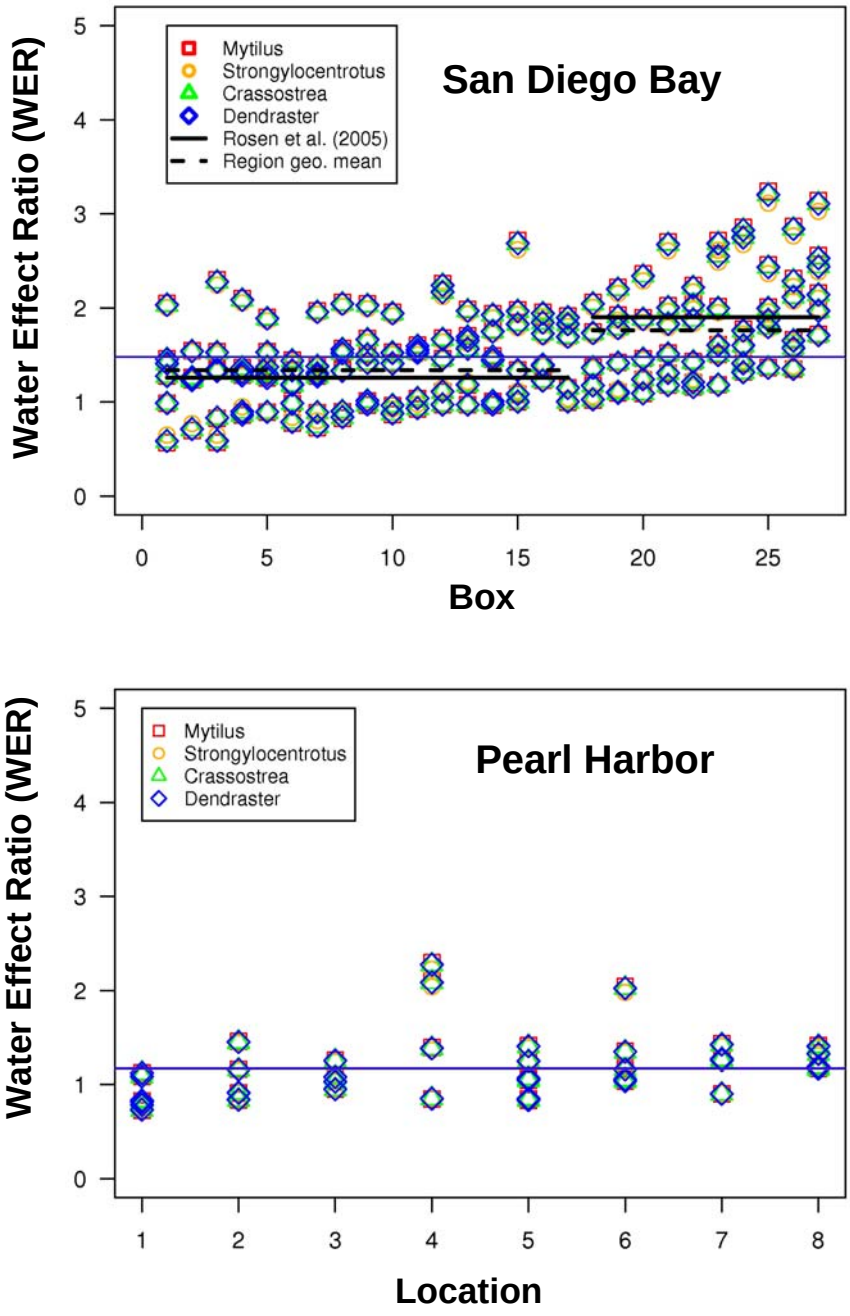


Figure 82. WER predicted with site-specific chemistry from San Diego Bay (top) and Pearl Harbor (bottom). Lines across the plots show the predicted geometric mean for each organism (Table 16). For San Diego Bay the two black lines are the geometric means reported by Rosen et al. (2005) for North (1.26) and South (1.90), and the corresponding broken lines are the predicted geometric means, 1.336 and 1.761, respectively.

Table 16. Predicted WER for San Diego Bay and Pearl Harbor. Values are geometric means followed by range in parentheses.

Site	Organism	WER
San Diego	*M. galloprovincialis*	1.483 (0.568 to 3.24)
	S. purpuratus	1.476 (0.649 to 3.11)
	C. gigas	1.479 (0.584 to 3.21)
	D. excentricus	1.478 (0.586 to 3.20)
	Overall	1.479
Pearl Harbor	*M. galloprovincialis*	1.174 (0.725 to 2.87)
	S. purpuratus	1.168 (0.761 to 2.74)
	C. gigas	1.172 (0.732 to 2.84)
	D. excentricus	1.172 (0.733 to 2.83)
	Overall	1.172

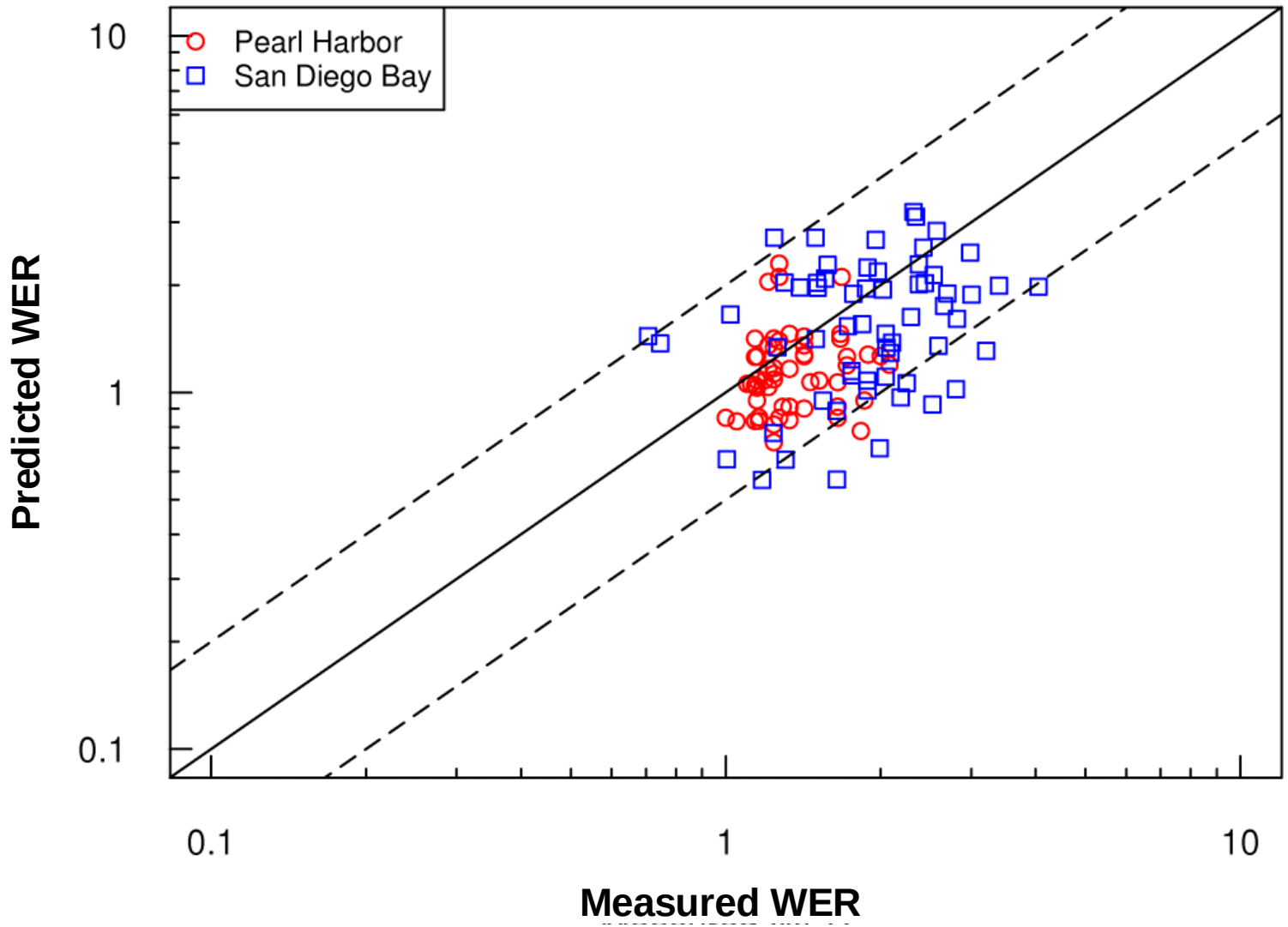


Figure 83. Comparison between WERs predicted by the integrated model and measured in San Diego Bay and Pearl Harbor.

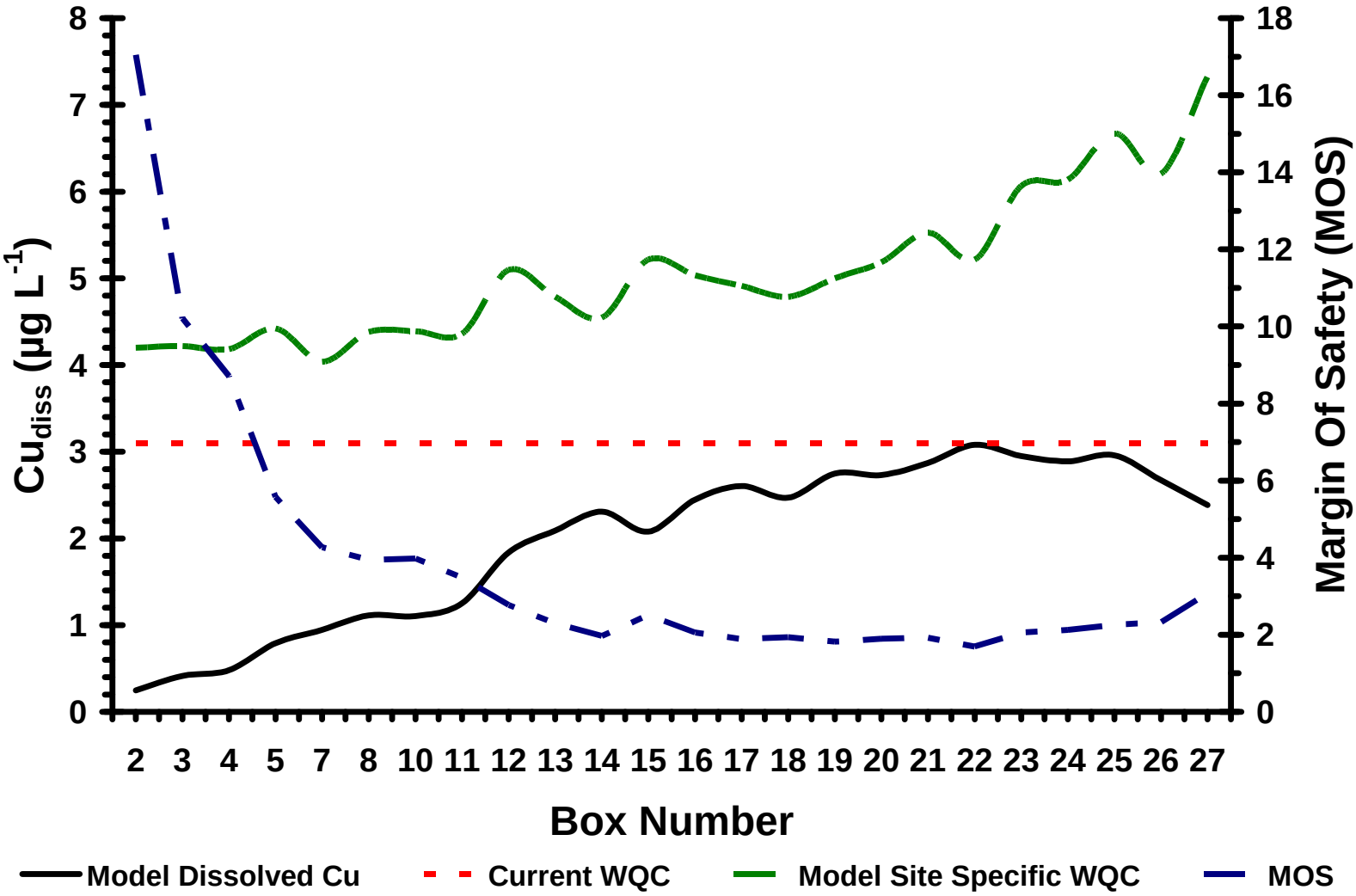


Figure 84. Relief predicted by the integrated CH3D/seawater-BLM model with a site-specific WQC for San Diego Bay. The MOS is the ×-fold increase in Cu_{diss} required to reach the toxicity threshold.

5. COST ASSESSMENT

5.1 COST REPORTING

The analysis and reporting costs associated with the development of the integrated model in San Diego Bay and Pearl Harbor were done by tracking costs and comparing them to those associated with the development of a WER and an F&T model (CH3D) in another DoD harbor with similar dimensions and characteristics as San Diego Bay. These analyses and reporting could not follow the Environmental Cost Analysis Methodology developed by the National Defense Center for Environmental Excellence (NDCEE, 1999). The actual costs incurred in the development of the San Diego Bay integrated CH3D/seawater-BLM model are shown in Table 17. Table 18 and Table 19 represent costs predicted for the application and development of CH3D and a WER in a harbor with similar dimensions and characteristics than San Diego Bay. These tables follow the Federal Remediation Technologies Roundtable guidance (FRTR, 1998).

The actual costs incurred in the demonstration of the San Diego Bay integrated CH3D/seawater-BLM model (Table 17) are categorized according to tasks required for the demonstration. The section on Operation and Maintenance is included for guidance; however, no actual costs are associated to this section, as the demonstration required a single validation of the integrated model. Funding for the presentation and discussion of the use of the seawater-BLM for regulatory purposes is included to promote the acceptance of this model by U.S. EPA. The total cost for the demonstration in San Diego Bay is $580,000.

The costs for implementation of an F&T model (CH3D; Table 18) are used for comparison with developing the integrated model. The integrated model provides a geographic distribution of toxicity and regulatory standards in the harbor. Similar distributions can be achieved by implementing a WER and an F&T model separately, and combining the results from each model generating the same information. Therefore, the costs of this technology demonstration is compared to the costs expected for the applications of these two combined efforts. The costs for implementing the CH3D in a harbor with similar size and characteristics as San Diego Bay are calculated at $128,583 (Table 18).

The costs associated with the development of a WER for a harbor similar in size and characteristics to San Diego Bay (Table 19) include only those expected for toxicity testing and associated measurement of Cu concentrations. There is no set value associated with the number of stations for WER development, but Federal guidance (U.S. EPA, 2001) indicates that the stations selected should be representative of the body of water. The WERs calculated by Rosen et al. (2005) for San Diego Bay are within a factor of three, suggesting that they are similar enough at both ends of the bay for regulatory purposes. However, if all samples in this study were collected near the back of the bay, the site-specific criterion would not be protective of areas near the mouth of the bay. This information directed on calculating the costs for eight stations distributed throughout the bay, and to characterize the toxicity (EC50) in two sampling events, to distinguish between dry and wet seasons. These costs are based on the current procedure at SSC Pacific for determination of EC50s, with seven different Cu concentrations in the aliquots for toxicity testing in each sample. Costs of measurement of Cu_{diss} and Cu_{tot} in each of these aliquots by ICP-MS utilizing a commercial laboratory are used. Development of a WER following the U.S. EPA recommended procedure (U.S. EPA, 2001) in this hypothetical harbor is estimated at $200,722.

Table 17. Actual costs incurred in the development and application of an integrated CH3D/BLM model for San Diego Bay.

Cost Category	Sub-Category	Cost ($)
Fixed Costs		
1. Capital Costs	Planning/Preparation[8]	34,800
	Set-up of CH3D	21,667
	Bioaccumulation studies	32,500
	Materials/Consumables[9]	24,750
	Calibration of CH3D	33,000
	Validation of CH3D	62,500
	Set-up of seawater-BLM	45,000
	Calibration of seawater-BLM	45,000
	Validation of seawater-BLM	45,000
	Integration CH3D + seawater-BLM	48,750
	Calibration of integrated model	66,000
	Validation of integrated model	62,500
	Other – Management support	27,083
	Other – Reporting	23,200
	Sub–Total	571,750
Variable Costs		
2. Operation And Maintenance	Integrated model run	(16,500)
	Model/document maintenance	(5,417)
	Reporting requirements	(11,600)
	Sub–Total	0
3. Other Technology - Specific Costs	Presentation/discussion for regulatory enforcement	8,250
	Sub–Total	8,250
	Total Technology Cost	580,000

The total costs for independent implementation of a WER and an F&T model for a harbor of similar dimensions and characteristics as San Diego Bay is estimated at $329,305 (Table 21), which is $250,695 less than the costs incurred during the development and demonstration of the integrated model in San Diego Bay (Table 21). The costs for implementation of the integrated model in a harbor of similar dimensions and characteristics as San Diego Bay is estimated at $189,567 (Table 20), which is $139,738 less than an independent implementation of a WER and F&T model (Table 21). If the user only selects the application of the seawater-BLM, the total estimated cost would be $60,894. The cost estimate for implementing the integrated model assumes that ancillary data required for the CH3D and seawater-BLM models are available. Sampling and analysis for these parameters will increase the projected costs.

[8] Labor was estimated at the rate for a federally employed scientist in FY08 of $104.86.
[9] These include materials used for copper larval bioaccumulation studies, and analysis of samples.

Table 18. Costs expected for the development and application of CH3D model in a new harbor with similar dimensions and characteristics as San Diego Bay.

Cost Category	Sub-Category	Cost ($)
Fixed Costs		
1. Capital Costs	Planning/Preparation	11,600
	Set-up of CH3D	21,667
	Materials/Consumables	2,475
	Calibration of CH3D	33,000
	Validation of CH3D	31,250
	Other – Management support	5,417
	Other – Reporting	11,600
	Sub–Total	117,008
Variable Costs		
2. Operation And Maintenance	Reporting requirements	5,800
	Sub–Total	5,800
3. Other Technology - Specific Costs	Presentation/discussion for regulatory enforcement	5,575
	Sub–Total	5,575
	Total Technology Cost	128,583

5.2 COST ANALYSIS

The major cost drivers for implementing the integrated model are on setting up and calibrating the models, which are fixed costs. These procedures are required to ensure that the information predicted is realistic for the harbor conditions. Once the integrated model is calibrated, minimum costs are required for operation and maintenance ($33,517, Table 20). The integrated model allows for modification and improvement on the F&T and toxicity prediction capabilities, and should evolve and mature with harbor conditions. In addition to being a tool for WQS estimation and verification, the integrated model helps on the allocation of best management practices on sources, and can forecast the resulting effects in the harbor. These expected savings are difficult to predict, and they vary amongst harbors.

Costs associated with eliminating regulatory fines by implementing attainable WQS with the integrated model are similar to those provided by implementing a WER. The main savings with the integrated model are related to the higher spatial and temporal resolution of environmental parameters, and the ability to use the model as a management tool for regulatory control.

Table 19. Costs associated with field development of a WER for a DoD harbor of similar dimensions as San Diego Bay. The predicted effort is for eight sampling stations, two sampling events (wet and dry seasons), and only include the costs required for determination of toxic points (EC50), without any further biological, physical, or chemical characterization of the bay.

Cost Category	Sub-Category	Cost ($)
Fixed Costs		
1. Capital Costs	Planning/Preparation	15,000
	Sampling	4,000
	Toxicity testing	40,000
	Chemical measurements (Cu_{diss})	28,000
	Chemical measurements (Cu_{tot})	28,000
	Other – Management support	3,000
	Other – Reporting	8,389
	Sub–Total	126,389
Variable Costs		
2. Operation And Maintenance	Labor	29,361
	Vessel rental/maintenance	6,000
	Laboratory maintenance	3,000
	Result analysis	8,389
	Model / document maintenance	4,194
	Reporting requirements	8,389
	Sub–Total	59,333
3. Other Technology - Specific Costs	Presentation/discussion for regulatory enforcement	15,000
	Sub–Total	15,000
	Total Technology Cost	200,722
	Unit Cost Per Sample	12,545

Table 20. Costs estimated for the implementation of the integrated CH3D/seawater-BLM model in another DoD Harbor.

Cost Category	Sub-Category	Cost ($)
Fixed Costs		
1. Capital Costs	Planning/Preparation	23,200
	Set-up of CH3D	21,667
	Materials/Consumables	2,475
	Integrated model se-up/run	21,667
	Calibration of integrated model	33,000
	Validation of integrated model	31,250
	Other – Management support	5,417
	Other – Reporting	11,600
	Sub–Total	150,275
Variable Costs		
2. Operation And Maintenance	Integrated model run	16,500
	Model/document maintenance	5,417
	Reporting requirements	11,600
	Sub–Total	33,517
3. Other Technology - Specific Costs	Presentation/discussion for regulatory enforcement	5,575
	Sub–Total	5,575
	Total Technology Cost	189,567

Table 21. Summary of costs incurred for the demonstration in San Diego Bay (actual) and for implementation of different models in a harbor similar to San Diego Bay.

Activity	Cost ($)	Cost Difference ($)
Demonstration San Diego Bay (actual)	580,000	
Difference actual San Diego Bay – (CH3D + WER)		250,695
Implementation of F&T Model CH3D in New Harbor	128,583	
Implementation of WER in New Harbor	200,722	
Total expected costs CH3D + WER	329,305	
Implementation of Integrated Model in New Harbor	189,567	
Difference (CH3D + WER) – Integrated Model		139,738
Implementation of seawater-BLM in New Harbor	60,894	

6. IMPLEMENTATION ISSUES

6.1 ENVIRONMENTAL CHECKLIST

As indicated above, the project objective is to demonstrate an Integrated CH3D/seawater-BLM model that will provide an improved methodology for achieving compliance for copper in San Diego Bay and other DoD harbors (i.e., development of TMDLs, site-specific WQS, and WERs) in a manner consistent with the current regulatory framework recently released for copper in freshwater systems (U.S. EPA, 2007). Therefore, although no waste stream emission will result from this project, the Federal regulations that pertain to this study include the WQC (U.S. EPA, 2007) and the NPDES program (U.S. EPA, 1999b).

6.2 OTHER REGULATORY ISSUES

Collaboration will be sought from regulatory and regulated agencies to facilitate the process of regulatory acceptance of the Integrated CH3D/seawater-BLM model. We are in the process of implementing an interagency memorandum between the U.S. EPA, the Army Corps of Engineers, and the Navy to collaborate in developing the integrated model. This collaboration will help the process for acceptance of the developed model. As stated in a Letter of Support for the proposal, Cindy Roberts from the U.S. EPA Office of Water indicated EPA's interest in the development of BLM modeling capabilities for sensitive saltwater toxicity endpoints, and in the improvement of our understanding of the F&T of copper in complex marine environments. Similar interests were expressed in a Letter of Support from Robert Ambrose from the U.S. EPA National Exposure Research Laboratory. Interest in the development of the integrated model within the Navy is expressed in the Letters of Support from S. S. Rupp, Commander of the Puget Sound Naval Shipyard and Intermediate Facility, and from Peter A. Kennedy, Deputy Assistant Chief of Staff, Environmental Department, Navy Region Southwest.

6.3 END-USER ISSUES

A primary concern with the Integrated CH3D/seawater-BLM model is the acceptance by stakeholders and regulatory agencies. There could be persistency and interest in continuing the approach of empirical evaluation of WERs and TMDLs, as opposed to applying the integrated model. This concern will be approached by performing and documenting a rigorous validation of the integrated CH3D/seawater-BLM model. This concern will also be approached by collaboration with U.S. EPA, DoD agencies other than the Navy, and private consultants (HydroQual, TetraTech).

Favorable and rapid acceptance is expected of the integrated model, as it is essentially an amendment to the commonly used CH3D and BLM models, both of which have been extensively used by regulated community and accepted by regulatory agencies as validated tools. Both models are amendable for model integration. Therefore, a relatively rapid acceptance and application of the integrated model should be expected, considering the developed seawater-BLM as an amendment for CH3D.

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APPENDIX A
ANALYTICAL METHODS SUPPORTING THE EXPERIMENTAL DESIGN

Table A-1. Analytical methods supporting the experimental design.

Parameter	Method	Reference
Sampling	Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels	U.S. EPA, 1996b
Sample handling and acidification	Trace-metal clean techniques, in HEPA Class-100 all-polypropylene working areas	
Cu_{tot}, Cu_{diss},	Liquid–liquid pre-concentration and analysis by U.S. EPA Method 7211, Copper by Atomic Absorption, Furnace Technique.	Bruland et al., 1985; U.S. EPA, 1992
Cu^{2+}	Direct measurement with Cu-ISE	Rivera-Duarte and Zirino, 2004
TOC, DOC	High-temperature combustion total organic carbon analyzer	Qian and Mopper, 1996
TSS	Filtration of 1L of sample thru glass fiber filters, rinsing and weighing of retained particles	
Salinity	Direct measurement with a Seabird 19 CTD	Lewis, 1980
Alkalinity and Total CO2	Acid titration in specially designed cell	Hernandez-Ayon et al., 1999
Cu-CC	Complexometric titrations with Cu-ISE	Rivera-Duarte and Zirino, 2004
Accumulation	Direct measurement of copper accumulation by larvae of sensitive organisms following a modified version of the U.S. EPA method for estimating chronic toxicity to Pacific coast marine and estuarine organisms	Rosen et al., 2008; U.S. EPA, 1995

APPENDIX C
QUALITY ASSURANCE PROJECT PLAN

C.1. PURPOSE AND SCOPE OF THE PLAN

To maintain an adequate quantity and quality of data for the integrated model demonstration, the Quality Assurance/Quality Control (QA/QC) Plan documents the results of the technical planning process, providing a clear, concise, and complete plan for the environmental data operation and its quality objectives, and identifying key project personnel (U.S. EPA, 2002). Careful adherence to these procedures ensures that demonstration data meet the desired performance objectives and yield appropriate analytical and modeling results.

C.2. QUALITY ASSURANCE RESPONSIBILITIES

The team that performed the demonstration is responsible for ensuring that the QA/QC Plan is implemented as written and approved. The members of the team are part of SSC Pacific or HydroQual. Bart Chadwick has primary responsibility for execution of the demonstration (SSC San Diego). The personnel responsible for bioaccumulation studies are Gunther Rosen and Ignacio Rivera-Duarte (SSC Pacific); for calibration and validation of seawater-BLM are Robert Santore, Adam Ryan, and Paul Paquin (HydroQual); and for calibration of CH3D is P. -F. Wang (SSC Pacific). P. -F. Wang (SSC Pacific) and Robert Santore (HydroQual) shared the responsibility for the integration of the two models, and calibration and validation of the integrated model. The quality assurance (QA) officer is Mr. Ernie Arias, who coordinated all QA activities, monitor methods, and records throughout the demonstration and data analysis; reviewed the data reduction and validation, and prepared and signed a statement specifying the findings.

C.3. DATA QUALITY PARAMETERS

As indicated in Section 3, there is an extensive suite of parameters required for development of WER, TMDL, and implementation of CH3D, seawater-BLM, and the Integrated CH3D/seawater-BLM models. Two different options were used for the gathering of the needed data: some data were from existing sources and some were developed as part of this demonstration. Most of the data already available was part of SERDP Project CP-1156 or Earley et al. (2007). The only new measurements included in this effort were those of the accumulation of copper by larvae of sensitive organisms (Rosen et al., 2008).

U.S. EPA (2002) describes the evaluation process for existing data. This process includes the following procedures: (1) to determine the data needs of the project, (2) to identify the data sources that might meet the project needs, (3) to evaluate the existing data in relation to the data quality specifications of the project, and (4) to document the quality issues in the final report.

The bioaccumulation study provided data needed for the development of the seawater-BLM. The quality of the data generated for these measurements was affected by the sampling and analytical techniques used; therefore, state-of-the-art trace metal clean techniques were used in sampling and analysis. Sampling was done following U.S. EPA Method 1669 (U.S. EPA, 1996b) on Sampling Ambient Water for Trace Metals, as the use of these techniques ensures the representativeness of the samples. Furthermore, the use of trace metal clean techniques and SRMs in the analysis of the samples provided information with respect to the quality parameters of the data. These data quality parameters are the precision, bias, accuracy, representativeness, comparability, completeness, and

sensitivity, which are defined and measured as described in the following subsections (U.S. EPA, 2002):

Precision is the agreement among repeated measurements of the same property under identical or substantially similar conditions. It is calculated either as the range or as the standard deviation. However, it may also be expressed as a percentage of the mean of the measurements, such as relative range or relative standard deviation (CV). Precision is quantified by using the same analytical instrument to make repeated analyses on the same sample, or by splitting a sample in the field and submitting both subsamples for sample handling, preservation and storage, and analytical measurements. The two options for the estimation of precision were used in our studies.

Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction. This distortion is quantified with the use of SRMs, or by analysis of spiked matrix samples. SRM 1643d of the National Institute of Standards & Technology was used to check for bias in the GFAAS analysis.

Accuracy is a measure of the overall agreement of a measurement to a known value, and includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations. Accuracy is quantified with SRMs or by repetitive analysis of spiked samples with known concentration, and it is usually expressed either as percent recovery or as a percent bias. In the case of the GFAAS analyses, the SRM 1643d of the National Institute of Standards & Technology was used to check for accuracy, and was reported as percent recovery.

Representativeness is a qualitative term that expresses "the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition." It is evaluated by the consistency of the data in comparison with historical data for locations with similar characteristics.

Comparability is a qualitative term that expresses the measure of confidence that one data set can be compared to another and can be combined for the decision(s) to be made. It is qualified by the similarity of sampling collection and handling methods, sample preparation and analytical procedures, holding times, stability issues, and QA protocols.

Completeness is a measure of the amount of valid data needed to be obtained from a measurement system, which is accomplished by comparing the number of valid measurements completed (samples collected or samples analyzed) with those established by the project's quality criteria.

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest, which is quantified as the minimum concentration that can be measured by a method (method detection limit), by an instrument (instrument detection limit), or by a laboratory (quantization limit).

C.4. CALIBRATION PROCEDURES, QUALITY CONTROL CHECKS, AND CORRECTIVE ACTION

Measurement of the copper concentration accumulated by the larva was done by direct injection of diluted samples into a GFAAS in accordance with U.S. EPA Method 7211 (U.S. EPA, 1992). These measurements were done by injections in triplicate for each sample, with relative standard deviation in the absorbance measured of less than 10%. To correct for matrix interferences, the method of standard additions was followed in the analysis, with a minimal acceptable correlation coefficient (r)

of 0.999 to ensure a good precision for the analysis. The SRM 1643d was included to check for the precision, bias, and accuracy of the analysis. This SRM was analyzed every five samples, and the analysis was accepted only when the recovery for this SRM was within ±15% of the certified value. High purity water (18 MΩ cm^{-1}) was also analyzed every five samples for the estimation of the method detection limit. At least one sample was analyzed in duplicate for every GFAA run, which provided information on the precision of the analysis.

For the bioaccumulation studies, duplicate samples at every concentration were sampled, and provided data for estimating the precision of the measurements and evidence of the representativeness of the data. Among these concentrations, the initial no-spiked concentration was sampled in quadruplicates to ensure the precision of the measurement at the lowest level. The reported data are given as the mean ±1 standard deviation to indicate the precision of the data.

C.5. DEMONSTRATION PROCEDURE

The demonstration required several different tasks. These tasks included the determination of the copper accumulation by larva of sensitive organisms, the calibration of a seawater-based BLM, the calibration of CH3D, the integration of the two models, the calibration of the integrated model, and the demonstration of the integrated model. In the beginning, several tasks were carried on simultaneously, including the larval accumulation study, development and calibration of seawater-BLM, and calibration of CH3D. Once these tasks were completed, then the integration of the two models was done. Initially, the integration was done externally, this is, the information from CH3D was provided to seawater-BLM, and the modeled results from seawater-BLM were provided back to CH3D for reporting. Once the results from both models were proved correct, then an internal integration started. The result of this integration was a unique model that could evaluate WER in accordance with actual regulation. There are six suites of data for San Diego Bay; four of them were used for the calibration of the models, and the other two sets of data were used for validation. For Pearl Harbor there are four suites of data, and three were used for calibration and one suite was used for validation.

C.6. CALCULATION OF DATA QUALITY INDICATORS

The quality of the measurements required for the evaluation of bioaccumulation and toxicity factors were evaluated following accepted U.S. EPA methodology (U.S. EPA, 2006). All of the data quality parameters are based in commonly used statistical calculations, including the determination of the mean value, the standard deviation, and the coefficient of variation. The calculation of these parameters was done in accordance with the following (U.S. EPA, 2006).

The sample mean or average ($\overline{X}$) is calculated as follows:

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i .$$

The sample variance (s^2) is required for the calculation of the standard deviation (s), and is calculated in accordance with this equation:

$$s^2 = \frac{\sum_{i=1}^{n} X_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} X_i\right)^2}{n-1} .$$

The sample standard deviation (s) is used as a measure of the precision of the measurements, and is calculated from the variance as follows:

$$s = \sqrt{s^2} \ .$$

The standard deviation of either duplicate samples or duplicate GFAAS analysis of the same sample was provided as evidence of the precision of the analysis. The standard deviation of high purity water (18 MΩ cm^{-1}) blank replicates was used to estimate the sensitivity of the method, as the method detection limit and the quantization limit. The method detection limit was calculated as three times the standard deviation of the blanks, and the quantization limit was defined as ten times the standard deviation of the blanks.

Another measure of the precision of the analysis is the coefficient of variation (CV), which is the ratio of the standard deviation (s) to the mean, and is calculated as follows:

$$CV = \frac{s}{\overline{X}} = \frac{\left[\frac{1}{n-1}\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2\right]^{1/2}}{\frac{1}{n}\sum_{i=1}^{n} X_i}.$$

In the method of standard additions for GFAAS measurements, it is critical to establish the response of the instrument to additions of the analyte to the sample. This task is accomplished with the Pearson's correlation coefficient (r), which is calculated as follows:

$$r = \frac{\sum_{i=1}^{n} X_i Y_i - \frac{\sum_{i=1}^{n} X_i \sum_{i=1}^{n} Y_i}{n}}{\left[\left[\sum_{i=1}^{n} X_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right]\left[\sum_{i=1}^{n} Y_i^2 - \frac{\left(\sum_{i=1}^{n} Y_i\right)^2}{n}\right]\right]^{1/2}}.$$

Bias and accuracy of the analysis were measured as percent recovery of SRM 1643d. This SRM was analyzed every five samples on each of the GFAAS runs, and the mean value measured was compared to the reported copper concentration of 20.5 ± 3.8 µg L^{-1}. The accuracy of the analysis was assessed by ensuring that the measured mean recovery is within 15% of the reported concentration. The bias of the measurement was assessed by ensuring that all of the measurements are within the same 15% recovery limits.

C.7. PERFORMANCE AND SYSTEM AUDIT

This section describes the types of audits that may have been conducted, appropriate corrective action procedures that were taken in the event of problems in the laboratory, and QA reports to management. Quality assurance audits evaluate the capability and performance of a measurement system or its components, and identify problems that warrant correction. Audits may include reviews of project plan adherence, training status, health and safety procedures, activity performance and records, budget status, QC data, calibrations, conformance to SOPs, and compliance with laws, regulations, policies, and procedures. Personnel, who are independent of the sampling and analytical

teams, conduct internal audits. Copies of audit reports were forwarded to the Principal Investigator. This section describes laboratory system, and performance audits.

System Audits include a thorough evaluation of laboratory QC procedures and are normally completed before data are collected. This type of audit may consist of site reviews of measurement systems, including facilities, equipment, and personnel. In addition, measurement, QC, and documentation procedures may be evaluated. System audits are conducted on a regularly scheduled basis; the first audit is conducted shortly after a system becomes operational.

Performance Audits review the existing project and QC data to determine the accuracy of a total measurement system or a component of the system. Performance audits of sampling and analysis procedures were conducted for laboratory activities.

Corrective Action Procedures, when **r**apid and effective, minimize the possibility that questionable data or documentation. An effective QA program requires prompt and thorough correction of nonconformance conditions affecting quality.

Two types of corrective actions exist: immediate and long term. Immediate corrective actions include correction of documentation deficiencies or errors, repair of inaccurate instrumentation, or correction of inadequate procedures. Often, the source of the problem is obvious and can be corrected at the time of the observation. Long-term corrective actions are designed to eliminate the sources of problems. Examples of long-term corrective actions are correction of systematic errors in sampling or analysis, and correction of procedures producing questionable results. Corrections can be made through additional personnel training, instrument replacement, or procedural improvements. One or more corrections may be necessary.

All QA problems and corrective actions were documented to provide a complete record of QA activities and to help to identify needed long-term corrective actions. Defined responsibilities are required for scheduling, performing, documenting, and ensuring the effectiveness of the corrective action.

Internal laboratory corrective action procedures and a description of out-of control situations requiring corrective action are contained in the laboratory QA plan. At a minimum, corrective action are implemented when any of the following three conditions occurs: control chart warning or control limits are exceeded; method QC requirements are not met; or sample holding times are exceeded. Out-of-control situations were reported to the program manager within 2 working days of identification. In addition, a corrective action report, signed by the laboratory director or project managers and the laboratory QA coordinator were provided to the program manager.

C.8. QUALITY ASSURANCE REPORTS

A quality assurance report will not be submitted as this is part of the previous efforts that provided the data used in this demonstration. In accordance with U.S. EPA (2002) regulations, the QA Plan includes the following plan elements:

1. Project Management
    - 1.1. Title Sheet
    - 1.2. Table of Contents
    - 1.3. Distribution List
    - 1.4. Project/Task Organization
    - 1.5. Problem Definition and Background

1.6. Project/Task Description
1.7. Quality Objectives and Criteria
1.8. Special Training/ Certifications
1.9. Documentation and Records

2. Data Generation and Acquisition
2.1. Sampling Process Design and Experimental Design
2.2. Sampling Methods
2.3. Sample Handling and Custody
2.4. Analytical Methods
2.5. Quality Control
2.6. Instrument/Equipment Testing, Inspection and Maintenance
2.7. Instrument/Equipment Calibration and Frequency
2.8. Inspection/Acceptance of Supplies and Consumables
2.9. Non-direct Measurements
2.10. Data Management

3. Assessment and Oversight
3.1. Assessments and Response Actions
3.2. Reports to Management

4. Data Validation and Usability
4.1. Data Review, Verification, and Validation
4.2. Verification and Validation Methods
4.3. Reconciliation with User Requirements

C.9. ISO 14001

The Environmental Management System (EMS) implemented at SSC Pacific was followed throughout the demonstration. This EMS complies with Navy EMS requirements, which follow the ISO 14001 International Standard. The following are five key elements on this EMS:

1. Environmental Policy at SSC Pacific:
1.1. Comply with all applicable environmental regulations
1.2. Minimize environmental impacts by preventing or reducing pollution
1.3. Strive to continually improve our environmental performance

2. Impact on the environment:
2.1. Some of the ways our processes/activities impact the environment are:
2.1.1. Computers and lights use up energy
2.1.2. Waste paper not recycled can fill up our landfills
2.1.3. Processes (like painting, cleaning and vehicle maintenance) use hazardous materials (HM) which create air emissions, produce wastewater, or generate hazardous waste (HW)

3. Pollution Prevention (P2) Plan to reduce environmental impacts:

3.1. Analyzes processes for potential reductions in HM usage and/or HW generation

3.2. Identifies P2 solutions for these processes

3.3. Assesses the feasibility of implementing these solutions

3.4. Implements the solutions

4. Specific objectives and targets for significant minimization of SSC Pacific environmental impacts:

4.1. Reduce solid waste generation by 25% by December 2008 by identifying recycling opportunities and increasing two-sided printing

4.2. Increase procurement of paper with 100% recycled content with 100% compliance by December 2006

4.3. Reduce overall energy usage by 35% by December 2010 by turning off lights and equipment when not in use and participating in Facilities Office projects to install more energy-efficient lighting

5. Procedures for dealing with emergency situations

5.1. If there is an emergency beyond your control:

5.1.1. Call 9911 (in rapid succession with no pause between the 9's) from a safe location. This will connect you with the Federal Fire Department.

5.1.2. If on a cell phone, call 911. When the person answers, inform them you are calling from a Navy facility. They will then connect you with the Federal Fire Department.

While these elements are very general, and apply for whole personnel at SSC San Diego, the elements that specifically affect the demonstration plan were strictly followed. These are those regarding the use and disposal of hazardous materials, and those concerning the safety of our personnel.

C.10. DATA FORMAT

Most of the measured data are stored as tables. However, scatter plots or any other form of representation or analysis was used as required. The results from the models are presented either as tables, scatter plots, time period plots, contour plots/maps. These formats were used as required for the analysis of the results and validation of the data.

C.11. DATA STORAGE AND ARCHIVING PROCEDURES

All final data were stored electronically. The storage media includes hard-disk memory, external hard disk, CD-ROM, and flashpoint memory. A folder as main central information depository is kept at the share-system at SSC Pacific. In contrast to the final data, the raw data are kept in laboratory notebooks, which include notes for each specific experiment, and for any problem identified in the experiment.

REPORT DOCUMENTATION PAGE

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OMB No. 0704-01-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
December 2008	Final	

4. TITLE AND SUBTITLE

DEMONSTRATION OF AN INTEGRATED COMPLIANCE MODEL FOR PREDICTING COPPER FATE AND EFFECTS IN DOD HARBORS

ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM (ESTCP)

Project ER-0523

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14. ABSTRACT

The Environmental Security Technology Certification Program supported Project ER-0523 on the demonstration of an integrated modeling system that provides an improved methodology for achieving copper compliance in harbors. This model is consistent with the current regulatory framework based on the Biotic Ligand Model (BLM) for freshwater. The integrated model has two components, the seawater-BLM (developed as part of this project), and the existing hydrodynamic transport and fate algorithm, Curvilinear Hydrodynamics in Three Dimensions model. The integrated model is applied at a harbor-wide scale, and accounts for the natural physical, chemical, biological, and toxicological characteristics of the harbor to achieve more scientifically based, cost-effective compliance. The integrated model is also a management tool for the optimization of efforts on source control, as it is robust enough for forecasting effects of controls on copper concentration and any associated toxicity in the harbor resulting from these controls. The integrated model was demonstrated in San Diego Bay and Pearl Harbor. In both harbors, the spatial and temporal distributions of copper species, toxic effects, and Water-Effect Ratio predicted by the integrated model are comparable to previously measured data. These results substantiate the support by the U.S. Environmental Protection Agency for future incorporation of the seawater-BLM in a full-strength seawater criterion. In San Diego Bay, the integrated model estimates that there is a safety factor of two between the actual copper concentrations and the predicted site-specific water quality standards (WQS), indicating that application of the predicted site-specific WQS will result in achievable discharge limits while providing the level of protection intended by the Clean Water Act. This demonstration contributes to the transition of this technology to the user community by providing a clear example of implementation at real-world Department of Defense sites.

15. SUBJECT TERMS

Mission Area: Environmental Science

fate and transport, water quality criteria, biotic ligand model
water quality standards, copper toxicity, compliance

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